This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

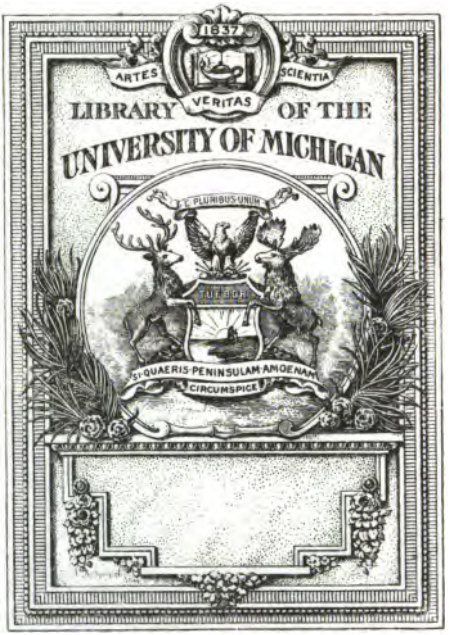
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`


1837
ARTES
SCIENTIA
VERITAS
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
TUEBOR
si QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

Chemical Library
QD
541
.D17

7/6

SOLUTION AND ELECTROLYSIS.

London: C. J. CLAY AND SONS,
CAMBRIDGE UNIVERSITY PRESS WAREHOUSE,
AVE MARIA LANE.

AND

H. K. LEWIS,
136, GOWER STREET, W.C.

Leipzig: F. A. BROCKHAUS.
New York: MACMILLAN AND CO.

Cambridge Natural Science Manuals.
PHYSICAL SERIES.

GENERAL EDITOR:—R. T. GLAZEBROOK, M.A., F.R.S.
ASSISTANT DIRECTOR OF THE CAVENDISH LABORATORY,
FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

SOLUTION AND ELECTROLYSIS

BY

WILLIAM CECIL DAMPIER WHETHAM, M.A.
FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

CAMBRIDGE:
AT THE UNIVERSITY PRESS.
1895

[*All Rights reserved.*]

Cambridge:
PRINTED BY J. & C. F. CLAY,
AT THE UNIVERSITY PRESS.

COLUMBIA UNIV.
Rec'd 4-7-31/MEN

PREFACE.

IN the following account of the phenomena of Solution and Electrolysis an attempt has been made to separate the description of the facts of the subject, and of the necessary theoretical consequences of those facts, from the consideration of the hypotheses which have been framed in order to explain them. It would be inconvenient, however, to adhere strictly to such a plan. Many experimental investigations, which have been undertaken by the light of the dissociation theory, would, although they may be explicable in other ways, have merely bewildered the reader, had he no working hypothesis to guide him through the maze of their detail. For an account of many such investigations the last chapter, which deals with theories of Electrolysis, must, therefore, be consulted. Nevertheless, the broad experimental outlines of the subject are sketched in the earlier part of the book, and theoretical ideas, except those which necessarily follow from the facts, are only provisionally introduced.

A considerable part of the matter of the first six chapters has been taken from the second edition of Professor Ostwald's *Lehrbuch der Allgemeinen Chemie*, the portion of which dealing with solutions has been translated into

English by Mr Pattison Muir. For a fuller account of the developments of the dissociation theory, the reader must be referred to the second volume of that *Lehrbuch*, and to Professor Nernst's *Theoretische Chemie*, an English translation of which, by Professor C. S. Palmer, has just appeared.

A complete description of all work on electrolysis, which appeared previously to 1883, will be found in Wiedemann's *Electricität*, and useful summaries appear in the Reports of the British Association for the years 1885, 1886, 1887 and 1890.

Those wishing to consult the original papers will find references to them in the following pages. In order to give clearness to chronological ideas, the date of each paper is given.

A valuable collection of data on the conductivities and migration constants of solutions was made by the Rev. T. C. Fitzpatrick, and published by the British Association in 1893. By the kind permission of the author and of the Council of the British Association, I have been allowed to reprint these tables as an appendix to this book.

My best thanks are due to Mr R. T. Glazebrook and Mr J. W. Capstick for their kindness in reading the proofs, and for the many valuable criticisms and suggestions they have made.

TRINITY COLLEGE, CAMBRIDGE.
May 22, 1895.

CONTENTS.

CHAP.		PAGE
I.	INTRODUCTION	1
	Properties of Solution. Range of the Subject.	
II.	SOLUTIONS IN GASES	8
	Solutions of Gases in Gases. Solutions of Liquids in Gases. Solutions of Solids in Gases.	
III.	SOLUTIONS IN LIQUIDS. SOLUBILITY	10
	Solubility of Gases in Liquids. Measurement of Solubility. Henry's Law. Solutions of Gases in Salt Solutions. Solubility of Liquids in Liquids. Solubility of Solids in Liquids. Influence of Pressure on the Solubility of Solids. Influence of Temperature. Analogy between Solution and Evaporation. Solubility of Mixtures. Solubility in Mixed Liquids. Table of Solubilities.	
IV.	DIFFUSION AND OSMOTIC PRESSURE	32
	General Principles of Diffusion. Osmotic Pressure. Application of the Gaseous Laws to Solutions. Application of Thermodynamics. Diffusion through Liquids. Experiments on Diffusion. Dialysis.	
V.	FREEZING POINTS OF SOLUTIONS	54
	Historical. Connection with Osmotic Pressure and other Theoretical Considerations. Experimental Methods. Determination of Molecular Weight. Influence of Concentration. Cryohydrates. Melting Points of Alloys.	
VI.	VAPOUR PRESSURES OF SOLUTIONS	74
	Theoretical Considerations. Boiling Points. Experimental Methods. Influence of Concentration. Determination of Molecular Weights. Solutions of Gases in Liquids. Solutions of Liquids in Liquids.	
VII.	THE ELECTRICAL PROPERTIES OF SOLUTIONS . .	103
	Historical Sketch. Faraday's Laws. Polarisation. Accumulators. Primary Cells. Contact Difference of Potential. Source of the Energy of the Current, and Theory of the Voltaic Cell.	

CHAP. PAGE

VIII. ELECTRICAL PROPERTIES (*continued*) 127

The Nature of the Ions. Secondary Actions. Practical Applications of Electrolysis. Complex Ions. The Migration of the Ions. The Velocities of the Ions.

IX. ELECTRICAL PROPERTIES (*continued*) 143

Resistance of Electrolytes. Experimental Methods. Experimental Results. Consequences of Ohm's Law. Influence of Concentration on Conductivity. Dissociation Theory. Ionisation. Influence of Concentration on Ionisation. Resistance of Liquid Films. Electrical Endosmose.

X. CONNECTION BETWEEN ELECTRICAL AND OTHER PROPERTIES 162

Conductivity and Chemical Activity. Conductivity and Osmotic Pressure.

XI. THEORIES OF ELECTROLYSIS 170

Introduction. The Dissociation Theory. Chemical Properties. Independent Ionic Velocities. Densities of Salt Solutions. Colours of Salt Solutions. Other Properties. General considerations. Development of the Dissociation Theory. Dissociation of Mixed Solutions. General case of Chemical Equilibrium. Thermal Phenomena. Diffusion of Electrolytes in Solution. Contact Difference of Potential. Dissociation of Water. Function of the Solvent. Hydrate Theory of Solution. Conclusion.

APPENDIX 213

Freezing Points.

TABLE OF ELECTRO-CHEMICAL PROPERTIES OF AQUEOUS SOLUTIONS 215

INDEX 285

ERROR.

On page 28, second line,

for $\frac{dp}{dT} \cdot \frac{1}{\lambda} = \frac{\lambda}{RT^2}$

read $\frac{dp}{dT} \cdot \frac{1}{p} = \frac{\lambda}{RT^2}$.

CHAPTER I.

INTRODUCTION.

1. Properties of Solution. When common salt is placed in water, the crystals slowly disappear, and a *solution* of the salt in water is formed. The presence of the salt can easily be recognised by taste, and it can be regained in the solid form if the water is boiled away. In presence of the *solvent*, water, the cohesion of the molecules of salt in the crystals is in some way overcome, and they are able to form part of a perfectly homogeneous liquid. Let us study the changes which go on in such a case a little more closely. If we take a large mass of salt and add only a little water, after a time no more solid disappears. We now have what is called a saturated solution. If we apply heat, however, we shall find that as the temperature increases, the water is able to dissolve more salt (very little more of the particular substance we have chosen, but of some things much more)—thus the solubility depends on temperature. Now let the solution cool. Little crystals form in the liquid till, when the temperature has fallen to the point at which we began, exactly the same amount of salt as at first is

dissolved in the water. For each temperature there is a fixed and definite amount of salt in the same volume of a *saturated* solution, however that solution is prepared. It will be convenient to represent this on a diagram. Let us divide OX, the horizontal axis of our figure, into 100 equal lengths to represent degrees on the Centigrade thermometric scale, and OY the vertical axis into 100 equal lengths to represent the parts by weight of salt which will

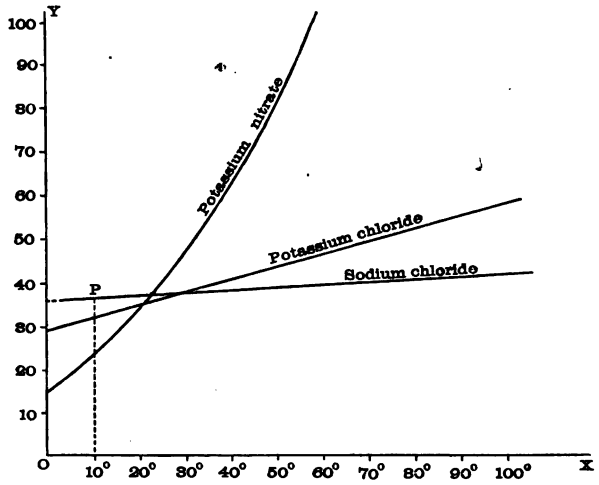


Fig. 1.

dissolve in 100 parts of water. Let us then make a series of measurements at intervals of 10 degrees of the mass of salt in a solution saturated at each temperature. Suppose we find that at 10° Cent. 35·7 grammes of salt are dissolved in 100 grammes of water. From the point marked 10° in the line OX let us draw a straight line

vertically upwards, and from the point corresponding to 35·7 in OY a straight line horizontally to the right. These lines meet in the point P which evidently completely expresses the amount of salt dissolved by 100 grammes of water to form a saturated solution at 10° C. If we do the same at temperatures of 20°, 30°, &c. we get a series of points, and if these are all joined by a smooth line, we get what is called a "Solubility Curve"—that is a curve shewing the way in which the solubility of the salt varies with the temperature. In the figure three such curves are given, shewing the solubility in water of the three substances, sodium chloride (common salt), potassium chloride and potassium nitrate. It will be seen that the three curves are very different. Not only are the solubilities of the three salts different at any one temperature, but the curve for potassium chloride, and still more that for potassium nitrate, is more steeply inclined than the curve for sodium chloride, shewing that the solubility of the two potassium salts increases more for a given rise of temperature than does that of the sodium salt.

When we dissolve sodium chloride in water an absorption of heat is observed. That is to say, if both salt and water when separate are at the temperature of the air, after the solution is formed its temperature is lower. On the other hand caustic potash gives an evolution of heat on dissolving and the temperature rises. During solution there are usually changes in *volume*. In all but rare cases contraction occurs, and the volume of the resultant solution is less than the sum of the volumes of the solvent and the substance dissolved, or *solvend*.

The boiling point of a salt solution is higher than that of pure water; and when it is remembered that a liquid boils when the pressure of its vapour is equal to the atmospheric pressure acting on it, we see at once that this statement is equivalent to saying that the vapour pressure of water is reduced by the dissolved salt. The steam which comes off however is the steam of pure water and will be found to assume the temperature at which pure water boils. Thermometers are graduated by marking on them the places at which the mercury stands at the freezing point and boiling point of water. It will be now seen why it is necessary during the latter operation to put the instrument in the steam and not in the water, which may contain impurities and be consequently boiling at a temperature slightly above 100° C.—its normal boiling point. Closely connected with this lowering of the vapour pressure is the lowering of the freezing point also produced by the substance in solution. Thus salt water does not freeze at a temperature low enough to solidify fresh water. Here again it is important to observe that the ice frozen out is the ice of pure water. Sometimes, particularly if the process of freezing has been rapid, particles of solid salt are shut in by the ice, and therefore redissolve when it is melted, but they are quite distinctly separated from the solid ice and never crystallize out in combination with it.

Many solutions are found to be good conductors of electricity, but in all such cases the passage of the current is accompanied by certain chemical changes, the dissolved substance being in general decomposed into two parts, one

of which is set free at the *anode*—the place at which the current enters the liquid—and the other appearing at the *kathode*, where it leaves. These liberated components often attack the solvent, and secondary chemical actions go on, so that the body finally liberated is not always the same as that primarily formed by the action of the current. The main body of the solution is apparently unaltered, all the products of decomposition appearing at the electrodes.

In this book we shall examine in greater detail these and other properties of solutions, point out how far they can be correlated and shewn to depend on one another, and consider their bearing on the question of the nature of the process.

2. Range of the Subject. The popular use of the term solution is restricted to the substances formed when solids dissolve in liquids, but many pairs of liquids will form mixtures which have properties exactly analogous to those described in the first section. Thus sulphuric acid and water are miscible together in all proportions, and the resultant body can be regarded either as a solution of sulphuric acid in water or of water in sulphuric acid. Many gases too are readily absorbed by liquids, and form solutions in which their properties are to some extent retained. Examples which will readily occur to everyone are ammonia and hydrochloric acid; while the fact that fish can breathe under water shews that even atmospheric air is to some extent soluble in that medium.

Many metals, such as silver and gold, will dissolve in the liquid metal mercury to form amalgams or alloys which exhibit many of the properties we have

described above as characteristic of solutions, and even alloys which are solid at ordinary temperatures, such as compounds of various metals with sodium or with tin, must be put in the same group.

We can if we like consider mixtures of gases as solutions of one in the other, thus getting an ideally simple case, undisturbed by many factors which influence the properties of the more complicated structures to which the term solution was at first restricted.

Ostwald defines solutions to be "homogeneous mixtures which cannot be separated into their constituent parts by mechanical means." Unless we read more meaning into the word "mixtures" than it usually implies, this would include all chemical compounds, and, although no definite line can be drawn between the processes of solution and chemical action, such a result would be inconvenient for purposes of classification. Chemical compounds are distinguished by constancy of composition, and their elements unite in definite proportions. Thus water is produced when two volumes of hydrogen unite with one of oxygen. If a little oxygen is present in excess we get, not a new compound, but water and uncombined oxygen. In the case of solutions however the constituents need not exist in any particular proportion. Thus if we have a solution of one molecule of sulphuric acid in three molecules of water, we can gradually add either sulphuric acid or water, and get gradual changes in the properties of the resultant liquid. This could of course be explained by saying that another definite compound was formed (say $H_2SO_4 . 4H_2O$), and that

intermediate solutions consisted of mixtures of this with the original $H_2SO_4\,3H_2O$, in the same way that we could prepare mixtures of water and hydric peroxide whose percentage composition should be anything we liked between that of the two oxides of hydrogen. The number of chemical compounds of two elements is however in general small, while in the case of solutions (especially of pairs of liquids miscible in all proportions) we should often have to suppose that a great many were possible. These considerations enable us to frame a definition which will, in the present stage of our knowledge, comprise exclusively those bodies we call solutions.

DEFINITION. *Solutions are homogeneous mixtures which cannot be separated into their constituent parts by mechanical means, the proportion between the parts being continuously variable between certain limits, with a corresponding continuous variation in properties.*

We shall begin by considering solutions in gases, and then the simpler cases of solution in liquids, leaving till later an account of the more complicated substances formed by dissolving mineral salts and acids in water. This will prevent any attempt to treat the subject historically, for, as is so often the case, the most obvious is not the most simple, and much trouble was needed, and many misleading threads were followed, before this tangled skein shewed any signs of becoming unravelled.

CHAPTER II.

SOLUTIONS IN GASES.

3. Solutions of Gases in Gases. Two gases which do not chemically interact can always form a homogeneous mixture with each other in all proportions. In the ideal case of two perfect gases all the properties of the mixture would be accurately the sum of those of the constituents. For instance, if the volume be kept constant the pressure of the mixture would be equal to the sum of the pressures exerted by each gas, while if the pressure be kept constant the resultant volume would be the sum of the individual volumes. In any real case these relations are only approximately fulfilled, the deviations becoming greater as the gases, either by cold or pressure, are brought nearer their points of liquefaction. These gaseous laws are obeyed by any matter existing in a finely divided state in which the particles are too far apart to exert any appreciable influence on each other for the greater part of the time. The physical properties then depend only on the number of particles and are independent of their nature. Cases which approach this will be found in dilute solutions in liquids, though here the influence of the solvent can seldom be neglected.

4. Solutions of Liquids in Gases. When a liquid evaporates into a space already filled with a gas, a solution of the vapour in the gas may be supposed to be present. As an approximate law Dalton found that the quantity of vapour in a given space was finally the same as if the space had originally been a vacuum, so that the final pressure was the sum of the pressure of the gas and the vapour pressure of the liquid. Regnault[1], Galitzine[2] and others have shewn that the vapour pressure of a liquid in a gas is in general less than in a vacuum, the deviations depending on the nature of the liquid and gas, as well as on their conditions of temperature, pressure, &c. Some of the gas may dissolve in the liquid and lower its vapour pressure, just as any other kind of dissolved matter—salt for example—would do. This must also be considered, as well as the forces between the molecules of the gas and vapour.

5. Solutions of Solids in Gases. Some solids will sublime without going through a liquid condition, and it is probable that laws similar to those just described hold good in these cases. Sometimes, under the influence of a gas at high pressure, a solid will sublime at a lower temperature than that usually necessary, thus forming a solution of a solid in a gas.

[1] *Mém. de l'Acad.* 26, p. 679.
[2] *Dissertation*, Strassburg, 1890.

CHAPTER III.

SOLUTIONS IN LIQUIDS. SOLUBILITY.

6. Solubility of Gases in Liquids. It appears that every gas is to some extent soluble in every liquid, though immense differences in solubility occur. When the amount dissolved has been great, it is generally found that chemical action has gone on, and the gas cannot be completely expelled by lowering the pressure, or increasing the temperature. As an example of this we may take the case of hydrochloric acid dissolved in water. On the other hand air, oxygen, hydrogen and other slightly soluble gases can be completely removed; the process of solution seems to be purely mechanical. But even in these cases the solvent exerts a selective influence, the gases differing from each other in solubility.

Let us examine these cases in which there seems to be no chemical action. The mass of a gas like oxygen which will dissolve in a given mass of water, is proportional to the pressure of the gas, or since the volume of a given mass of gas varies inversely as its pressure, the *volume* which goes into solution, measured under the pressure to which it is subject in the liquid, is the same whatever be the pressure. The reason of this law is at once

evident if we consider what the mechanism of the process must be. Molecules of gas must strike the surface of the liquid and some must be retained, either by molecular forces or by a process of entanglement or both. When the number of these becomes great, some of them will reach the surface from the body of the liquid with such an energy of motion, and under such conditions, that they are once more able to fly off into the gas. When the number so leaving the solution in any given time is equal to the number entering it from without, equilibrium is maintained, and the solution has become saturated with the gas. If the pressure is reduced, the number of gaseous molecules striking the liquid, and therefore the number per second retained by it, are reduced in the same proportion, while the rate at which they leave is at first unchanged. The concentration of the gas in solution is thus gradually lowered till equilibrium is again attained, and the concentration bears once more its old relation to the external pressure. At first sight it would appear that the solubility of a gas should be unaffected by an alteration of temperature, since the number of molecules impinging on the surface from within and without would be changed in the same proportion. But here the influence of the solvent comes in, and the molecular forces between it and the gaseous molecules are reduced by increase of temperature so that the solubility becomes less. It is found that, in general, the solution of a gas in water, even when the liquid is nearly saturated, is accompanied by an evolution of heat. From this it follows by the principles of thermodynamics (see p. 26), that the solu-

bility will decrease with rising temperature. The fact that heat is evolved in the solution of gases in water is of great interest, for the state of a substance in solution more nearly approaches its state when gasified than when either liquid or solid, so that during the process of solution of a *gas* less change goes on in the state of physical aggregation than in other cases. This has been brought forward as evidence in favour of the view that solution is in all cases a chemical process, resulting in the formation of definite liquid hydrates[1].

7. Measurement of Solubility. In an experimental determination of solubility it is necessary to take precautions to ensure complete saturation, as the process of diffusion of matter from one portion of a liquid to another is very slow. Many forms of apparatus have been devised, the simplest being that used by Bunsen[2], who placed a measured volume of the gas in a graduated tube over mercury and added a certain volume of the liquid. The tube was then shaken in a water bath of constant temperature, the open end being screwed against an india-rubber plate. By repeatedly opening the end under mercury and then closing it again and shaking, saturation was obtained, the solubility being determined by measuring the volume of gas left over, the volume of the liquid, and the final pressure.

The *solubility* of a gas has been defined by Ostwald[3] to be the ratio of the volume of gas absorbed to the

[1] See Pickering, Watts' *Dictionary of Chemistry*, Art. Solution II.

[2] *Pogg. Ann.* 1855, 93, p. 10.

[3] *Lehrbuch der allg. Chemie.*

volume of the absorbing liquid, at any specified temperature and pressure, or

$$\lambda = \frac{v}{V}.$$

Bunsen used a more complicated property, which he called the *absorption coefficient.* It is obtained from Ostwald's "solubility" by reducing the volume of gas absorbed to 0° C. at the pressure of the experiment. In the cases in which no chemical action occurs, we have seen that the *volume* of gas absorbed is independent of the pressure, so that if β is Bunsen's absorption coefficient, and a the coefficient of gaseous expansion

$$\lambda = \beta(1 + at).$$

Bunsen and others have determined many absorption coefficients for water and alcohol. The following are some of their results[1]:

	Hydrogen		Oxygen		Carbon Dioxide	
Temp.	In Water	In Alcohol	In Water	In Alcohol	In Water	In Alcohol
0°	0·0215	0·0693	0·0489	0·2337	1·797	4·330
15°	0·0190	0·0673	0·0342	0·2232	1·002	3·199

8. Henry's Law. The law that the mass of a gas dissolved is proportional to the pressure was given by Henry[2], who established it as an approximation by a series of experiments on five gases at pressures varying from one to three atmospheres. Bunsen made more accurate observations, both by varying the pressure in his absorpti-

[1] Bunsen, *Pogg. Ann.*, 1855, 93, p. 10. Winkler, *Berichte*, 1889, 22, p. 1439. Timofejeff, *Zeitschr. f. physikal. Chem.* 1890, 6, p. 141.

[2] *Phil. Trans.* 1803.

ometer and by using a mixture of gases. If we have a volume of gas at atmospheric pressure, consisting of equal parts of two constituents, the total pressure is obviously due half to one and half to the other, so that, restricting our consideration to one gas, the pressure it exerts is half that of the atmosphere. In this way by using mixtures in which the proportion of one gas continually diminished, its pressure could be reduced from one atmosphere to zero, and it was found that the mass absorbed varied in the same proportion.

In the case of such very soluble gases as ammonia, the phenomena are not quite so simple, though at 100° C. the law of Henry holds good[1]. If observations be made at lower temperatures, however, the mass of ammonia absorbed is not proportional to the pressure, and the curve drawn to shew the variation of solubility with pressure when the temperature is kept at 0° C., shews two changes of curvature. Sulphur dioxide behaves like ammonia, the law only holding true above 40°. Hydrogen chloride cannot be entirely removed from solution in water either by reducing the pressure to zero or by boiling. If aqueous hydrochloric acid be distilled, its strength will either increase or diminish till a liquid of a certain composition remains, which distils over unchanged. This composition depends on the pressure at which the operation is carried on; at normal atmospheric pressure the proportion of hydrogen chloride is 20·24 per cent., at 50 mm. of mercury pressure the proportion is 23·2 per cent., and at 1800 mm. it sinks to 18 per cent.

[1] Sims, *Annalen*, 1861, 118, p. 345.

Thus deviations from Henry's law are found in the case of gases which are near their points of liquefaction, and therefore depart from Boyle's law, and also in cases in which chemical action obviously occurs.

9. Solutions of gases in salt solutions. The coefficient of absorption for a gas appears to be lowered when a salt which does not act chemically on the gas is previously dissolved in the water. In general, however, chemical action does occur, and the gas dissolved may be considered to consist of two parts—one being held chemically by the salt nearly independently of the pressure, and the other varying with the pressure in accordance with Henry's law. Good examples of this are seen when carbon dioxide is dissolved in a solution of sodium carbonate or disodium phosphate. Solutions of similar salts of equivalent strength absorb nearly equal quantities of carbon dioxide—*e.g.* the sulphates of zinc and magnesium[1].

The effect of mixing another liquid with the water is similar to that of dissolving a salt in it—the absorption coefficient for a gas is reduced. This holds even with such substances as sulphuric acid and alcohol, which are themselves in the pure state as good as or better than pure water in absorbing power. Thus with sulphuric acid Setschenoff found for carbon dioxide a minimum absorption coefficient when the composition of the liquid was $H_2SO_4.H_2O$. His results are as follows.

H_2SO_4	$H_2SO_4+\frac{1}{2}H_2O$	$H_2SO_4+H_2O$	$H_2SO_4+2H_2O$	$H_2SO_4+58H_2O$	H_2O
·923	·719	·666	·705	·857	·923

[1] Setschenoff, 1875, *Méms. de l'Akad. Pétersb.*, 22, No. 6; 1889, *Z. f. physikal. Chemie*, 4, p. 117.

These numbers shew that a mixture of sulphuric acid and water absorbs less carbon dioxide than either liquid does when pure. Similar relations are found to hold good for other physical properties, *e.g.* the electrical resistances and the viscosities.

10. Solubility of Liquids in Liquids. When we pass to the consideration of solutions of liquids in liquids we find that there are three classes into which pairs of liquids can be divided. Those in the first class are mutually soluble in all proportions; thus mixtures of alcohol and water, or of water and sulphuric acid, can be prepared of any composition. Those in the second class are soluble in each other but not in all proportions; thus water will dissolve about ten per cent. of ether, and ether about three per cent. of water, but if either substance be present in excess it separates out forming a definite layer. The third class consists of liquids which are insoluble in each other, but these are few, and under proper conditions every liquid appears to be to some extent soluble in every other liquid. The divisions between these classes are dependent on external conditions, thus liquids which are only partially miscible at ordinary temperatures may mix in all proportions when heated, and it is probable that all liquids approach the condition of complete miscibility as they approach their critical points[1].

Measurements of the mutual solubility of liquids have been made by Alexejeff[2], who placed weighed quantities

[1] It is stated (Watts' *Dict.*, Art. Solutions I.) that diethylamine and water, though miscible in all proportions at low temperatures, cease to be so when heated.

[2] *Wied. Ann.* 1886, 28, p. 305; *Chem. Centralblatt*, 1882, pp. 328, 677, 763.

in a sealed tube and noted the temperature at which the mixture became homogeneous.

The form of the solubility curve for a pair of partially miscible liquids is shewn in fig. 2, in which the abscissæ represent temperature and the ordinates percentages of dissolved substances in 100 parts of the solution. The

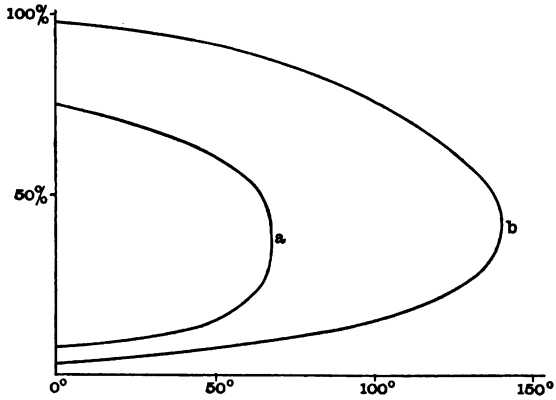


Fig. 2.

curve *a* represents a solution of water and phenol; the curve *b* water and aniline phenolate. At low temperatures there are two definite states in which equilibrium is attained—the lower branch of the curve representing a solution of phenol in water, the upper branch a solution of water in phenol.

11. Solubility of Solids in Liquids. Great differences in solubility are presented by various substances in the same liquid, and bodies which are quite insoluble in one liquid may be readily soluble in another. No satisfactory explanation of these differences can be given, though,

until this is possible, the essential nature of the process of solution must be regarded as imperfectly understood. It has been noticed that solution is more likely to occur if the solvent and solvend are chemically somewhat alike, than if they differ widely in their nature, (thus mineral salts and acids are in general most readily dissolved by water, while benzene is a more likely solvent for organic substances), but even in this sense no general rule can be framed. We must therefore be content in the present state of knowledge to study the phenomena of solubility without reference to the question of its fundamental nature.

If we have a large quantity of a solid in contact with a small quantity of liquid, solution will go on till a certain saturation point is reached. The proportion between liquid and solid in the solution, is then independent of the amount of solid which is present in excess, and depends only on the temperature, and, to a very slight extent, on the pressure. If there is insufficient solid to produce saturation, a more dilute solution is of course formed. On the other hand an abnormally great amount of dissolved substance can be retained, if the solvent be saturated at a higher temperature and the clear liquid poured off from the excess of solid and slowly cooled. We then get what is called a *Supersaturated Solution.* If a small crystal of the dissolved substance be dropped in, precipitation at once occurs, and a solution saturated at the temperature of the experiment is left. Any crystal isomorphous with those of the dissolved body will produce the same effect. The phenomena are well seen in the case of Glauber's salt,

sodium sulphate, $Na_2SO_4.10H_2O$, supersaturated solutions of which can be obtained of such strength that the addition of a crystal of the salt causes the whole mass to solidify, and gives rise to a considerable increase of temperature. If a solution of this body be cooled to a low temperature, it deposits crystals whose composition is $Na_2SO_4.7H_2O$. If the temperature be still further lowered, more of these crystals appear, while if it be raised some of them redissolve. The solution is thus evidently saturated with regard to them, and a definite equilibrium is attained for each temperature. But the solution is all the time supersaturated with regard to Glauber's salt, and the introduction of a crystal of that salt will at once cause solidification. It is thus clear that the conditions of saturation involve an equilibrium between the solution and the solid, so that if one of these be removed the same conditions no longer hold. Measurements of various physical properties of non-saturated, saturated and supersaturated solutions have been made in order to find out whether any sudden change of properties in the liquid mark the point of saturation. Determinations of the electrical conductivity, freezing point, specific gravity, specific heat, heat of solution, rate of expansion, specific viscosity, and molecular volume, have shewn that none of these properties shew any abrupt change as the saturation point is reached and passed. There is therefore nothing abnormal in the state of a supersaturated solution as far as the liquid is concerned. This result confirms our conclusion that it is the absence of any solid in contact with the liquid that changes the conditions of equilibrium.

12. Influence of pressure on the solubility of solids. This is very small, and accurate experimental determinations are very difficult. The dynamical theory of heat indicates that the chief conditions determining the change of solubility with increasing pressure are the heat of solution of the salt in the nearly saturated solution, and the change in volume on solidification. The few experiments which have been made seem to confirm this conclusion.

13. Influence of temperature. Many investigations on the influence of temperature on the solubility of solids in liquids have been made from the time of Gay Lussac to the present day. The solubility is usually defined as the number of parts of the solid which can be dissolved in 100 parts of solvent. It is determined either by shaking up an excess of solid with the liquid till no more dissolves, or by dissolving at a higher temperature, and then allowing the solution to cool in contact with solid to the temperature at which the measurement is to be made. The quantity of dissolved substance is then determined either by evaporating and weighing the residue, or by chemical analysis. As a general rule solubility increases with temperature, though several exceptions to this rule are known, (e.g. calcium hydroxide, and sodium sulphate between the temperatures of 33° and 100°). It is impossible, when studying the influence of temperature on solubility, to miss seeing the analogy between the solution of a solid in a liquid and the evaporation of a liquid into a closed vacuous space. Just as for every temperature there is a definite quantity of vapour present in the space

when equilibrium is reached, so there is a definite quantity of solid dissolved. Increase of temperature causes in the one case more liquid to evaporate, and in the other more solid to dissolve, till a new state of equilibrium is reached. We shall see hereafter that just as a liquid exerts a vapour pressure, so a solid in solution exerts a *solution pressure* which can be recognised and measured by means of certain phenomena, to which the name of osmose has been given. The analogy between the two processes seems thus very close, and this is borne out by the general similarity of the solubility curves to curves which shew the variation of vapour pressure with temperature. As we remarked while studying supersaturated solutions, the equilibrium is between the solid and the solution; saturation occurs when the number of particles leaving the solid per second is equal to the number deposited by the solution. Any change in the nature of the solid, such as an alteration from the hydrated to the anhydrous form, or a change in the number of molecules of water in the hydrated molecule, upsets the equilibrium, and a new saturation point results.

Thus calcium sulphate, $CaSO_4$, is more soluble in water in the anhydrous form than as hydrated crystalline gypsum, $CaSO_4.2H_2O$. If we prepare a saturated solution of gypsum and bring it in contact with the anhydrous salt, it takes up more calcium sulphate. It thus becomes supersaturated with regard to gypsum, and would crystallise on the addition of a fragment of that substance.

Now it can be shewn in two ways that the body which

exists in solution is exactly the same whether it has been obtained from crystalline hydrated gypsum, or from anhydrous calcium sulphate. Firstly, none of the curves shewing the variation of the different physical properties (see p. 19) of the solution shew any change of curvature as the point of saturation for gypsum is passed, so that no new substance can have been introduced; and secondly, when a hydrated salt is dissolved, the water of hydration cannot be distinguished from the rest of the water by any difference in molecular volume or other physical property. It also follows from the densities of solutions and from their thermal capacities (see § 80) that the salt in solution affects the whole of the water together and equally. We are thus prevented from supposing that the solvent which contains as much hydrated gypsum as it can take up, has still the power of dissolving a certain quantity of anhydrous salt as such, and of keeping hydrated and anhydrous molecules simultaneously in solution. This again drives us back to the view that saturation is an affair of the solid as well as of the liquid in contact with it.

A most interesting example of these cases is found in the variation of the solubility of sodium sulphate with temperature. The solubility goes on increasing from 0° to 33°, but beyond that point it diminishes till a temperature of 100° is reached.

The explanation which was formerly given was that below 33° hydrated salt is present in solution, but that above 33° it is converted into the anhydrous state. No change in the physical properties of the solution can

however be detected, and the truth is that at 33° a change occurs in the *solid* which is in contact with the solution. The solubility up to 33° is that given by the equilibrium between a solution of sodium sulphate and the crystals $Na_2SO_4.10H_2O$ (Glauber's salt), above 33° the solubility is determined by the conditions of equilibrium between the solution of sodium sulphate and the solid anhydrous

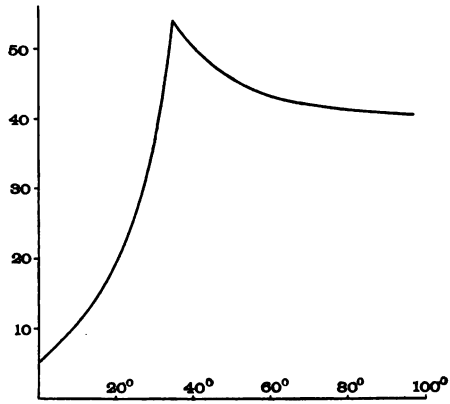


Fig. 3.

substance Na_2SO_4. The diagram (fig. 3) thus really consists of two distinct solubility curves, which cut each other at 33°. In the case of Thorium sulphate the hydrates are so stable that the course of both curves can be traced beyond their point of intersection[1].

A long series of investigations on the influence of temperature on solubility has been made by Étard and Engel[2], who find that many other sulphates agree with

[1] *Zeits. f. phys. Chemie*, 1890, 5, p. 198.

[2] *Comp. Rend.* 1884–8, 98, pp. 993, 1276, 1432; 104, p. 1614; 106, pp. 206, 740.

Glauber's salt in having maximum solubilities at definite temperatures, while certain calcium salts have minimum values.

If solubility be defined as the parts of salt in 100 parts of *solution*, instead of 100 parts of *solvent*, each part of the curve generally comes out as a straight line. Thus the curve for copper sulphate consists of three straight lines which meet at 55° and 105°.

As we have already remarked, the solubility increases or diminishes with rising temperature, according as heat is absorbed or evolved when some of the solvend dissolves in the nearly saturated solution, so that the thermal effect must change sign where maxima or minima occur in the solubility curve.

The phenomena of supersaturation are now seen to be quite comprehensible. When a liquid is cooled in contact with the solid which would be deposited from it, the precipitation goes on as the temperature sinks, so that equilibrium is just maintained. If no solid be present however, there is no reason for precipitation to occur, as one of the two bodies which exist in equilibrium in the usual case is absent. When the molecules of the dissolved substance get so close together that chance aggregations may produce crystalline structures of considerable size, spontaneous crystallization may occur. The phenomena suggest a comparison with the formation of water-drops in moist air, which has been found by Aitken to require the presence of dust particles or other nuclei for its initiation. Surface tension is the cause which retards the spontaneous formation of minute water-drops in clean air

saturated with water vapour. This gives to the drops an amount of potential energy proportional to their areas of free surface. For a given volume of water, the total area will be greater the smaller are the drops in which it is diffused. The precipitation of the excess of water in a mass of supersaturated air can only begin by the formation of very minute drops, and consequently the change might actually involve an increase in the total potential energy of the system. When this is the case spontaneous precipitation cannot occur, and the presence of nuclei is necessary.

The same cause may prevent the formation of permanent crystals by the chance aggregations of molecules of salt in a solution. The surface tension between solid and liquid may be sufficient to increase the potential energy and so prevent crystallization. If this explanation is a true one the surface tension between solid and liquid should be great in those cases which readily shew the phenomena of supersaturation[1].

14. Analogy between solution and evaporation. An expression connecting the temperature variation of vapour pressure with the latent heat of evaporation can be deduced by the application of the second law of thermodynamics, which states that in any cycle the ratio of the work done by a reversible heat engine, to the heat used by it, is the same as the ratio of the range of tem-

[1] An account of the principle of minimum potential in its application to solution and chemical action will be found in Liveing's "Chemical Equilibrium."

perature to the absolute temperature of the source of heat.

Let us suppose that we have in the cylinder of our engine some liquid in contact with its vapour at an absolute temperature $= T$. Let it expand isothermally till the volume has increased by dv, owing to the evaporation of one gram of liquid. If p is the vapour pressure, the work done is pdv, and the heat absorbed is the latent heat of vaporisation, λ. Then let the vapour expand adiabatically till its temperature sinks to $T - dT$. The pressure will now be $p - \frac{dp}{dT}dT$, and if we reduce the volume isothermally at the new temperature to its original value, the work done will be $\left(p - \frac{dp}{dT}dT\right)dv$. The balance of effective work done by the engine during the cycle will therefore be $pdv - \left(p - \frac{dp}{dT}dT\right)dv = \frac{dp}{dT}dT.dv$, and by the second law of thermodynamics we get

$$\frac{\frac{dp}{dT}dTdv}{\lambda} = \frac{dT}{T}$$

or

$$\frac{dp}{dT} = \frac{\lambda}{Tdv} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

The general analogy between evaporation and solution on which stress has already been laid (see p. 20), leads us to apply this equation to the process of solution. In this case p will represent either the solution pressure, which can be measured by osmosis (see Chap. IV.), or the concentration which is approximately proportional to it, dv is the volume

of solution in which one gram-molecule of the solvend is dissolved, and λ is the heat of solution of one gram-molecule in the saturated solution (that is the heat change involved in the passage of the solution from the state of saturation at a temperature $T - dT$ to the state of saturation at a temperature T). Since T and dv are both positive quantities, it follows from the equation that dp/dT, the rate of variation of concentration with temperature, and λ, the heat of solution, must have the same sign, so that if the solution of a substance is attended by an absorption of heat the solubility increases with temperature, if it is attended by an evolution of heat the solubility decreases.

This is a special case of the general law that when a system is controlled by two variables dependent on each other, a change in one of them produces a change in the other in such a direction that the change in the first is resisted.

In dilute solutions we shall find that the molecules of the dissolved substance obey Boyle's law, that is to say that the solution pressure which they produce is inversely proportional to the volume occupied. From the usual equation for Boyle's law

$$p \times \text{volume} = RT,$$

where R is a constant, we find that the volume is equal to RT/p.

If we substitute this value for the volume dv in our equation

$$\frac{dp}{dT} = \frac{\lambda}{Tdv}$$

it becomes $$\frac{dp}{dT} = \frac{\lambda p}{RT^2}$$

or $$\frac{dp}{dT} \cdot \frac{1}{\lambda} = \frac{\lambda}{RT^2}$$

$$\therefore \frac{d}{dT}(\log_e p) = \frac{\lambda}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2).$$

We can thus deduce λ, the heat of solution, from the solubility curve, and Van 't Hoff has given a table which shews a good agreement with the same constant determined experimentally. We shall shew in Chapter IV. how to calculate the value of the constant R for solutions.

	$\frac{\lambda}{1000}$ calculated	$\frac{\lambda}{1000}$ observed
Oxalic acid	8·2 calories	8·5 calories
Potassium bichromate	17·3 „	17·0 „
Amylic alcohol	− 3·1 „	− 2·8 „
Phenol	1·2 „	2·1 „
Alum	21·9 „	20·2 „
Potassium chlorate	11 „	10 „
Borax	27·4 „	25·8 „

The solubility curve cannot be deduced conversely from the heat of solution (though its direction can), for if we integrate the equation we get

$$\log_e p = \int \frac{\lambda dt}{RT^2} + \text{constant} \quad \ldots\ldots\ldots\ldots (3),$$

and this constant, which determines the absolute value of the solubility, remains unknown.

The fact that the solubility of a body is determined by the properties of the solid in contact with the solution, suggests that when the temperature is raised above the

melting point of the solid, a difference in solubility may result. But it can easily be shewn that although a difference in the direction of the curve may there begin, at the melting point the solubility of the liquid must be the same as that of the solid—the two curves must intersect. At the melting point liquid and solid can exist in contact at the same temperature. If we suppose one to be more soluble than the other, it will tend to produce a stronger solution than the other can support. Matter will therefore continually dissolve away from the more soluble body and will be deposited on the less soluble, and since one of these is solid and the other liquid, differences of temperature will be produced by the heat effect involved in change of state, in a system which was originally at a uniform temperature throughout. This is contrary to experience as formulated in the second law of thermodynamics. Thus at the melting point the solubility of the liquid must be the same as that of the solid. The difference between the solid and the liquid state can be considered as measured by the energy required to pass from one to the other, i.e. by the heat of fusion. This suggests that the angle at which the two solubility curves meet will be greater as the heat of fusion is greater. The exact relation can be deduced from the equations used above, and J. Walker[1] has confirmed the results experimentally.

15. Solubility of Mixtures. If water be shaken with a mixture of two salts, the solution when saturated is

[1] *Zeits. f. physikal. Chemie*, 1890, 5, p. 192.

in general found to contain less of each substance than it would have done if the other had been absent, though to this rule there are many exceptions.

In the case of salts which are not isomorphous and do not form double salts, the composition of the solution is independent of the proportion in which the solids are mixed, and of the method by which the solution is prepared. In the case of substances which form double salts, if we add excess of A to a saturated solution of B, the double salt separates out till a solution is formed which is saturated both as regards A and the double salt, and is not changed by a further addition of A. The third case, when the salts are isomorphous and can crystallize together in all proportions, gives saturated solutions whose compositions vary continuously with the composition of the solid mixture. By adding successive quantities of A it is possible to completely displace the salt B from the solution. Much experimental work has been done in this subject by Rüdolf[1], and Ostwald has pointed out the analogy between these phenomena and the vapour pressures of mixed liquids, the three cases given above corresponding to the cases (i) when the liquids do not mix, (ii) when they are partially miscible, (iii) when they are miscible in all proportions.

Nernst[2] has shewn that the solubility of a slightly soluble salt like silver acetate must be greater in pure water than in a solution of any other electrolyte which contains either silver or the acetate group. A corre-

[1] *Pogg. Ann.*, 1873, 148, pp. 456, 555. *Wied. Ann.*, 1885, 25, p. 626.
[2] *Zeits. f. physikal. Chemie*, 1889, 4, 372.

sponding phenomenon is observed in the case of gases which, like the vapour of NH_4SH, partially decompose. The partial pressures of the products of decomposition are less in the presence of either ammonia or sulphuretted hydrogen.

16. Solubility in mixed liquids. If a liquid is added to a solution with which it is miscible, the dissolved substance will be to some extent precipitated if it is insoluble in the liquid added. Thus copper sulphate or sodium chloride can be precipitated from their aqueous solutions by the addition of alcohol. No relation can however be traced between the amount precipitated and the quantity of alcohol added.

A dissolved body divides between two solvents in a constant ratio which is independent of the absolute concentration. This statement, which is deducible from the physical theory of solution, was confirmed for the solution of succinic acid in ether and water by Berthelot and Jungfleisch[1]. If the bodies have different molecular weights when dissolved in the two solvents, like benzoic acid in benzene and water, different laws hold good and these were investigated by Nernst[2].

17. Table of Solubilities.

Substance	Solvent	Solubility (parts in 100 parts of solvent) At 0°	At 20°	At 100°
Sodium chloride	Water	35·5	36·0	39·2
Silver nitrate	„	121·9	228·0	1111·0
Calcium sulphate	„	0·205	0·23	0·19
Barium chloride	„	31·0	35·7	58·8

[1] *Ann. de Chimie*, 1872, [4], 26, pp. 396. 408.

[2] *Zeits. f. physikal. Chemie*, 1891, 8, p. 110.

CHAPTER IV.

DIFFUSION AND OSMOTIC PRESSURE.

18. General Principles of Diffusion. When a mass of gas is placed in an empty vessel, it finally, if the small effects due to gravity be neglected, distributes itself equally throughout the volume. This at once follows from the molecular theory, for the particles of which the gas is composed are always moving about from one place to another. If then we suppose that an imaginary partition is placed anywhere in the gas, the number of molecules crossing it in one second from left to right will be proportional to the number present in unit volume (i.e. the *concentration*) on the left-hand side, and the number crossing from right to left proportional to the number per unit volume on the right. If the concentration is greater on one side than the other, more molecules will leave that side per second than enter it, and thus the concentration will be reduced till it is equal on both sides. A similar process goes on in the case of a substance dissolved in a liquid: uniformity of distribution is finally reached, though here the difficulties put in the paths of the dissolved molecules

by the presence of the solvent, prevent their travelling fast, and make the process of diffusion very slow.

In the case of mixed gases it is found that the final state of distribution of one gas is not affected by the presence of the other. Thus the amount of aqueous vapour which diffuses from water into a vacuum, is sensibly the same as if the empty space previously contained air, though in this case the process of diffusion is slower. This too is obviously a necessary consequence of the molecular theory, for, whether the air be present or not, equilibrium is reached when the number of molecules which leave the liquid per second is equal to the number returning to it from the vapour.

Collisions between the molecules are continually taking place, and thus the average energy of translation of each molecule becomes on the whole the same, though sometimes the molecule may be travelling faster and sometimes slower. This must also hold good even if the molecules are of different kinds, as in a mass of mixed gas—the average energy of each is still the same. The kinetic energy being one-half the mass multiplied by the square of the velocity, it follows that light molecules must travel faster than heavy ones and will therefore diffuse more quickly. This can be shewn by the familiar experiment of filling a closed porous pot with air and surrounding it by an atmosphere of hydrogen or coal gas. The molecules of hydrogen enter more rapidly than the heavier ones of air go out, and a pressure gauge will shew that the pressure inside the pot becomes greater than outside. If we could in any way entirely prevent the air from leaving, we could get a

permanent increase of pressure, for the hydrogen would enter till its concentration was the same within as without.

19. Osmotic Pressure. The corresponding phenomenon in the case of liquids is shewn by experiments on what is known as *osmotic pressure*. Pfeffer[1] shewed how to prepare membranes which readily allow pure water to pass, but are impervious to certain substances dissolved in it which do not act on the membrane. These *semi-permeable* membranes are made by filling a porous pot with the solution of a salt such as potassium ferrocyanide, and surrounding the outside with another solution—copper sulphate for example—which gives an insoluble precipitate when in contact with the first. The solutions gradually diffuse into the walls of the cell, and form an insoluble membrane on the surface along which they meet. The solutions are then washed out, and the membrane is complete. Let us place inside a pot so prepared a solution of some substance—cane sugar for example—and immerse it in pure water. The molecules of liquid will strike the walls of the membrane on both sides, but since there are both sugar and water molecules inside, fewer *water* molecules will, in a given time, hit the wall inside than outside. More water molecules pass in therefore, than go out, and, since none of the sugar can escape, an internal pressure is produced which can be measured by any convenient gauge. The process will go on until the pressure due to the water is the same on both sides,

[1] *Osmotische Untersuchungen*, Leipsic, 1877.

and thus the excess of pressure measured is equal to that due to the sugar alone. The case of sugar was chosen because little or no contraction in volume occurs when it is dissolved, or when the solution is diluted, which makes the theory of the subject much more simple. Here, at all events, there is strong evidence to shew that the simple physical explanation we have given is enough to account for the phenomena.

In most cases the osmotic pressure, as thus measured, will include other properties which cause a diminution in the potential energy of the system on dilution. There may be, for example, a change of volume, or chemical action between the solvent and the dissolved substance, as well as the pressure due to the motion of the molecules in solution. When equilibrium is obtained the potential energy of the whole system must have reached a minimum value.

20. Application of the Gaseous Laws to Solutions. When we measure the numerical value of this osmotic pressure we find that, in dilute solutions, the laws which regulate its value are the same as those which govern the behaviour of gases and vapours. The importance of these results was first pointed out by Van 't Hoff[1], who called attention to the fact that Pfeffer's measurements of the osmotic pressure of cane sugar proved that the pressure varied as the concentration, *i.e.* that it was inversely proportional to the volume occupied

[1] *Phil. Mag.*, 1888, 26, p. 81, or *Zeits. f. physikal. Chemie*, 1887, 1, p. 481.

by a given mass of sugar. This exactly corresponds to Boyle's law for gases. The following are some of Pfeffer's numbers.

Percentage of sugar in solution	Pressure in millimetres of mercury	Pressure calculated for one per cent. of sugar
1	538	538
1	532	532
2	1016	508
2·74	1513	554
4	2082	521
6	3075	513
1	535	535

The numbers in the last column are constant except for irregular experimental errors.

In the case of gases, Boyle's law fails to represent the accurate relation between pressure and volume at very great pressures, and it also fails for solutions when the concentration becomes considerable. We should expect the law of variation to be more complicated for solutions, since in addition to the intermolecular forces similar to those brought into play in the case of gases, we shall here have forces between the dissolved molecules and the solvent.

For dilute solutions, to which we shall at first restrict ourselves, the theory shews that the pressure should increase as the temperature rises; and that the variation should follow the laws of gases and make the pressure proportional to the absolute temperature. This result has not been fully confirmed experimentally, but Donders

and Hamburger[1] found that the variation in pressure due to temperature was independent of the nature of the dissolved substance. This corresponds to the fact that the coefficient of increase of pressure is the same for all gases. The method used was a comparative one, and shewed that solutions which were *isotonic* (*i.e.* gave equal osmotic pressures) at one temperature, 0°, were also isotonic at another, 34°.

It is found that the protoplasmic contents of certain organic cells are surrounded by a membrane which behaves like those prepared by Pfeffer in only allowing pure water to pass. If such a cell be placed in a concentrated salt solution, the more dilute cell sap parts with water faster than the external liquid, the contents of the cell contract and shrink away from the cell walls. If on the other hand the cell be placed in water, liquid passes in, and the membrane becomes stretched. By staining the contents of the cell and having a graduated series of solutions of varying strength, it is easy to find, by observations with a microscope, what strength of solutions gives equilibrium with the cell sap, and is therefore isotonic with it. Solutions of two different substances can thus be prepared so that both are isotonic with the contents of a given kind of cell, and (assuming that two solutions isotonic with a third are isotonic with each other) we can find the respective strengths of the two salt solutions which give equal osmotic pressures. De Vries[2], who was the first to use this method, employed vegetable cells.

[1] *Zeits. f. physikal. Chemie*, 1890, 6, p. 319.

[2] Pringsheim's *Jahrbücher*, 1884, 14, p. 427.

and Donders and Hamburger in their investigation on the influence of temperature used blood corpuscles.

De Vries established the most important generalisation, that solutions of different substances containing the same number of gram-molecules[1] in a given volume are isotonic. This is equivalent to saying that at equal pressures the solutions of all (non-electrolytic) substances contain, in a given volume, the same number of molecules, which corresponds to Avogadro's law for gases. Tammann[2] confirmed this by allowing a drop of copper sulphate solution to fall into a solution of a ferrocyanide. A little membrane is at once formed round the drop, and the concentrations of the solutions are altered till, when this is done, no water enters or leaves the cell. Whether any such passage went on or not was determined by noticing if there was any change in the index of refraction of the liquid just outside the little cell.

It is important to observe that in the case of solutions which are electrolytes (that is to say, which have the power of conveying a current of electricity and of undergoing simultaneous chemical decomposition), the osmotic pressure is greater than that given by the solution of a non-electrolyte containing the same number of gram-molecules in a given volume. Thus a table of the "isotonic coefficients" of some indifferent substances given by De Vries is as follows, the isotonic coefficient being a number representing the osmotic pressure when

[1] *Note*—A "gram-molecule" is the molecular weight of a substance in grams.

[2] *Wied. Ann.* 1888, 34, p. 299.

that of an equimolecular solution of potassium nitrate is taken as 3:

Cane sugar	1·81
Inverted sugar	1·88
Glycerine	1·78

while the coefficients of electrolytic solutions are greater:

Potassium nitrate	3·0
Sodium nitrate	3·0
Potassium chloride	3·0
Potassium sulphate	3·9
Potassium tartrate	3·99
Magnesium chloride	4·33
Calcium chloride	4·33

The importance of this phenomenon we shall examine in detail later.

When we pass on to the examination of the absolute value of the osmotic pressure, we find another striking relation to gaseous properties. We know that one gram of hydrogen or sixteen grams of oxygen, at normal atmospheric pressure and 0° C., occupy a volume of about 11·16 litres. Therefore one molecular weight of a gas in grams (2 grams of hydrogen or 32 grams of oxygen) occupies under these conditions a volume of 22·32 litres, or if compressed into one litre would, by Boyle's law, exert a pressure of 22·32 atmospheres. By Avogadro's law the same pressure would be exerted by any gas or vapour that was a considerable distance from its point of liquefaction.

The absolute values of osmotic pressures have been found by Pfeffer, Adie[1] and Tammann. Pfeffer found that

[1] *Chem. Soc. Jour. Proc.* 1891, p. 344.

at 6°·8 a one per cent. solution of sugar gave an osmotic pressure of 505 mm. of mercury. The molecular weight of cane sugar ($C_{12}H_{22}O_{11}$) is 342. Hence a one per cent. solution contains $\frac{10}{342}$ of a gram-molecule in one litre. A volume of hydrogen or of any other gas, which contained $\frac{10}{342}$ of a gram-molecule in one litre would at 6°·8 exert a pressure of

$$760 \times \frac{10}{342} \times 22{\cdot}32 \times \frac{279{\cdot}8}{273} = 508 \text{ mm. of mercury.}$$

Thus we find that in dilute solutions of indifferent substances

(i) The osmotic pressure is proportional to the concentration, that is, inversely proportional to the volume occupied by a given mass (Boyle's law).

(ii) The coefficient of *variation* of pressure with temperature is the same for all substances, and probably (though this is not fully established by experiment) the pressure is proportional to the absolute temperature (Gay Lussac's law).

(iii) Solutions which exert the same pressures contain the same number of dissolved molecules in a given volume (Avogadro's law).

(iv) The absolute value of the osmotic pressure of the solution of a non-electrolyte is the same as that of a gas or vapour containing the same number of molecules in a given volume.

Thus we find that the osmotic pressure of dilute solutions obeys all the gaseous laws, and has the same absolute value as it would have if the dissolved substance were transformed into a gas at the same temperature

without change of volume. We can therefore apply to solutions the usual equation which expresses the relation between the pressure p, and the volume v, of a gas, and write

$$pv = RT,$$

where T denotes the absolute temperature, and R is a constant whose value can be found as follows. Let us consider a mass of gas equal to its molecular weight in grams at 0° C. and 760 mm. pressure. The pressure is $76 \times 13{\cdot}6 \times 981 = 1{\cdot}014 \times 10^6$ C.G.S. units, the volume, as we have seen on p. 39, is 22320 c.c. and the absolute temperature is 273°. We therefore get

$$R = \frac{pv}{T} = 8{\cdot}290 \times 10^7 \text{ ergs per degree centigrade}$$

or dividing by the mechanical equivalent of heat ($4{\cdot}2 \times 10^7$) we get in thermal units

$$R = 1{\cdot}974 \text{ or nearly 2 calories per degree.}$$

If we define the concentration of a solution to be the number of gram-molecules per cubic centimetre, it is equal to $1/v$, and we can write an equation for osmotic pressure in the form

$$p = cRT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4).$$

The real cause of this remarkable relation is the same as that which makes the gaseous laws independent of the composition of the different gases. Both in gases and in dilute solutions the molecules are in general so far apart that they are nearly always out of each other's range of influence, and only those properties which, like the pressure, depend on the number and not on the nature of the molecules, are brought into prominence, while those which

depend on the composition of the molecule tend to disappear. Properties which depend in this way only on the number of the particles and not on their nature are called *colligative properties*. The reason of this importance of the colligative properties at great dilution is at once seen if we remember that while properties which, like the pressure produced by impact, depend simply on the number of molecules, must be proportional to the concentration, properties which depend on the forces between the molecules must be proportional to the square of the concentration; for a new molecule added not only exerts force on others but also allows others to exert force on it. But any term which is proportional to the square of a quantity becomes very small, compared with a term depending on the first power, when the quantity becomes small, so that the term in the expression for the osmotic pressure which depends on intermolecular forces must be negligible at great dilution, compared with the term due to the impact of the molecules which is proportional to the concentration.

It would be quite possible to explain the fact that the *variation* of the osmotic pressure of solutions obeys all the gaseous laws, by the action of chemical forces between the dissolved substance and the solvent[1], but on that hypothesis there seems to be no particular reason why the osmotic pressure should assume the same *absolute* value as that which the dissolved molecules would give were they gasified. It is this last fact which seems to shew that in dilute solutions of indifferent bodies, the osmotic pressure is caused by molecular bombardment. The consideration

[1] See Fitzgerald, *B.A. Report*, 1890, pp. 142, 328.

of the case of salt solutions must be deferred till we have described the facts of electrolysis.

21. Application of Thermodynamics. The direct determination of osmotic pressure is a very difficult process, but we shall proceed to shew that there is a connection between this pressure and other properties of solutions—their vapour pressures, and freezing points. This connection is independent of the particular view we take of the cause of osmotic pressure, and can be deduced simply from the principles of thermodynamics. For most purposes therefore it is better to make experimental determinations of the freezing points, and deduce the corresponding value of the osmotic pressures. This is particularly advisable in the case of strong solutions, which would give osmotic pressures so large that a direct experimental determination would offer great difficulties. We shall therefore leave the account of the osmotic pressures of strong solutions with the deviations from the gaseous laws which they shew, till we have considered the freezing point determinations.

Van 't Hoff was the first to point out that the existence of osmotic pressure, to whatever cause it may be due, enables the laws of thermodynamics to be applied to solutions. For imagine the solution of some substance to be enclosed in a cylinder fitted with a piston, and having its bottom made of a semipermeable membrane. If it be placed in water, the volume of liquid inside will increase until the pressure on the membrane is just equal to the osmotic pressure, when equilibrium will be attained. If

in this state we heat the cylinder, the osmotic pressure is increased, more water will enter, and the piston will rise. If we cool it, the osmotic pressure falls, water is squeezed out, and the volume inside becomes less. On the other hand by increasing the pressure on the piston we can force out water and so reduce the volume, keeping the temperature constant, or by decreasing that pressure we can draw water in and make the volume greater. We have evidently a system which is in all respects analogous to a cylinder containing gas, and by keeping the pressure on the piston nearly equal to the opposing osmotic pressure, we can make all the above processes reversible, and obtain with solutions an apparatus which acts in all respects like Carnot's perfectly reversible heat engine.

This principle can be used to examine the relation between osmotic pressure and temperature. Beginning with the ideal machine described above in a state of equilibrium, let us reduce the pressure on the piston by an infinitely small amount, and so allow water to enter, and the piston to slowly rise—the temperature being kept constant by the addition of a quantity of heat whose mechanical equivalent is H. If the volume of water which enters is dv, and we neglect any contraction it may experience on mixing with the solution, the work done is $p\,dv$, and this must be equal to H. Let the piston still rise, with no further addition of heat. If the temperature sinks to $t-dt$ the pressure becomes $p-\frac{dp}{dt}\,dt$. The piston is then pushed in at this lower pressure till a change of volume equal to dv is produced, the heat being

removed so that the temperature keeps constant. Finally the removal of heat is stopped, and the piston is further pushed in till the original temperature and volume are regained. The work done *by* the engine at the higher temperature is as we have seen $p\,dv$, while that done *on* it at the lower temperature is $\left(p - \frac{dp}{dt}\,dt\right) dv$, so that the balance of available work obtained during the cycle is

$$p\,dv - \left(p - \frac{dp}{dt}\,dt\right) dv = \frac{dp}{dt}\,.\,dt\,dv.$$

Now by the laws of thermodynamics we know that the total amount of heat converted into work by a perfectly reversible engine, working between the temperatures t and $t - dt$, is to the amount of heat absorbed by the engine at the higher temperature, as the difference in temperatures is to the absolute temperature t,

$$\text{hence the work done} = H\,\frac{dt}{t}.$$

We therefore get

$$H\frac{dt}{t} = p\,.\,dv\,.\,\frac{dt}{t} = \frac{dp}{dt}\,.\,dt\,dv,$$

or

$$\frac{p}{t} = \frac{dp}{dt},$$

and by integration

$$p = Ct \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5),$$

where C is the integration constant.

Therefore the osmotic pressure of dilute solutions should be proportional to the absolute temperature.

22. Diffusion through Liquids. According to

the molecular theory then, diffusion is due to the motion of the molecules of the dissolved substance through the liquid. These molecules have momentum, and the osmotic pressure measures the rate at which this momentum is transferred across unit area. When the osmotic pressure is uniform throughout, the molecules will be uniformly distributed, but if the pressure varies from point to point the concentration will not be uniform. There must thus be a relation between the rate of change of the concentration and the variation of osmotic pressure, and this has been investigated by W. Nernst[1] and M. Planck[2]. Suppose we have a vertical cylinder with a solution of some non-electrolyte in its lower part, and pure water at the top. The dissolved substance gradually makes its way upwards through the water, and, neglecting the small disturbing effect of gravity, a uniform solution will finally result.

At a height x in the cylinder let the osmotic pressure be p, so that if q be the area of cross section, the substance in the layer whose volume is qdx, finds itself under the action of a force equal to $-qdp$, the negative sign being taken because the force acts in the direction in which the pressure *decreases*. If c be the concentration in gram-molecules per cubic centimetre, the force which in this layer acts on each gram-molecule is

$$-\frac{q}{cq}\frac{dp}{dx}=-\frac{1}{c}\frac{dp}{dx}.$$

Let k denote the force required to drive one gram-

[1] *Zeits. f. physikal. Chemie*, 1888, 2, p. 615.
[2] *Wied. Ann.*, 1890, 40, p. 561.

molecule through the solution with a velocity of one centimetre per second; then the velocity attained is

$$-\frac{1}{ck}\frac{dp}{dx},$$

and if dN be the number of gram-molecules which cross each layer in a time dt, since the number crossing unit area per second is proportional to the concentration and to the average velocity of the individual molecules, we get

$$dN = -\frac{1}{ck}\frac{dp}{dx}qc\,dt = \frac{1}{k}q\frac{dp}{dx}dt.$$

If the solution is dilute, and if there is no polymerisation or dissociation of molecules with change of concentration, we may apply equation (4) for the osmotic pressure, viz. $p = cRT$, the value of the constant R corresponding to one gram-molecule being again taken. This gives

$$dN = -\frac{RT}{k}q\frac{dc}{dx}dt \quad \ldots\ldots\ldots\ldots\ldots (6).$$

On the analogy between diffusion and the conduction of heat Fick[1] supposed that the quantity of substance which diffused through unit area in one second was proportional to the difference of concentration between that area and another parallel layer indefinitely near it. This difference in concentration is proportional to $-\frac{dc}{dx}$, so that the quantity crossing an area q in a time dt is

$$dN = -Dq\frac{dc}{dx}dt \quad \ldots\ldots\ldots\ldots\ldots (7),$$

where D is the "diffusion constant," and by comparison

[1] *Pogg. Ann.*, 1855, 94, p. 59.

with equation (6) is seen to correspond to the term $\frac{RT}{k}$. Fick's equation was fully confirmed by the work of H. F. Weber[1] (see p. 49), which therefore also supports the truth of the theory given above.

Owing to the slowness of the diffusion, the unit of time generally adopted for experimental work is the day instead of the second, so that the observed diffusion constant K is given by the expression

$$dN = -\frac{K}{86400} q \frac{dc}{dx} dt \quad \ldots\ldots\ldots\ldots\ldots (8),$$

$$\therefore \quad q \frac{dc}{dx} dt = -\frac{86400\, dN}{K}.$$

But from equation (6) we see that the force required to drive one gram-molecule through the solution with a velocity of one centimetre per second is

$$k = -\frac{RT}{dN} q \frac{dc}{dx} dt.$$

$$= \frac{86400\, RT}{K} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9).$$

Thus if we know K, the diffusion constant, we can calculate k, the force required to produce unit velocity. Voigtländer gives 0·472 as the diffusion constant of formic acid at 0° C., and from this we can calculate that the force required to drive one gram-molecule (46 grams) of formic acid through water with a velocity of one centimetre per second is equal to the weight of 4340 million kilograms. The reason such an enormous force is needed is at once seen if we remember the minute size of the molecules and

[1] *Wied. Ann.*, 1877, 2, p. 24.

the difficulties they must meet with in struggling through the liquid.

If the temperature be uniform, a solution will in the end become homogeneous, but if the upper layers be kept hotter than those below, in order that the osmotic pressure should be the same throughout, the concentration in the lower layers must become greater. This result was experimentally established by Soret[1] and the cause pointed out by Van 't Hoff[2].

23. Experiments on Diffusion. The first to make a thorough investigation of diffusion without a separating membrane was Graham[3], who covered a wide-mouthed bottle containing a solution with a large volume of water, and after some time measured the quantity of substance in the water. By this method Graham found that acids diffused about twice as quickly as normal salts, and that the rate of diffusion of these salts varied much according to their composition. Two salts together diffused independently of each other, so that it was possible to separate the constituents of some double salts, the alums for example, which were decomposed by water. The quantity which diffused was found to be nearly proportional to the concentration of the original solution, and to depend largely on the temperature.

Weber was the first to work out a satisfactory method of determining the absolute value of the diffusion constant in Fick's equation. When two plates of amalgamated

[1] *Ann. Chim. Phys.*, 1881, 22, p. 293.
[2] *Zeits. f. physikal. Chemie*, 1887, 1, p. 487.
[3] *Phil. Trans.*, 1850, pp. 1, 805; 1851, p. 483.

zinc are placed in two solutions of zinc sulphate of different concentrations, the solutions being in contact with each other, a difference of electrical potential is produced between the plates which is proportional to the difference in concentration, provided that difference is small. A concentrated solution of zinc sulphate was placed in the lower part of a cylindrical vessel, the bottom of which was made of an amalgamated zinc plate, and a dilute solution gently poured in on top of the first. The electromotive force between the lower zinc plate and a similar plate placed in the topmost layer of liquid was measured, and found to decrease as the difference in concentrations became less. If we apply Fick's law to this case we get an infinite series in the expression for the electromotive force, but if the time is long, the first term only is important; and we get, if H is the height of the vessel, and t the time

$$E = Ae^{-\frac{\pi^2}{H^2}Kt} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10).$$

The following table gives the observed values of $\frac{\pi^2}{H^2}K$, which should be constant if Fick's law holds good.

Days	$\frac{\pi^2}{H^2}K$
4—5	·2032
5—6	·2066
6—7	·2045
7—8	·2027
8—9	·2027
9—10	·2049
10—11	·2049
Mean	·2042

This complete verification of Fick's law also supports

the theory of diffusion given on p. 45, since that theory leads to a similar equation.

Fick's law can be put into another form if we take the case of a very long cylinder with the concentration at one end remaining constant. In this case Stefan[1] shewed that the quantity diffusing through an area q should be

$$a = cq\sqrt{\frac{Kt}{\pi}}.$$

To apply this to a finite cylinder we must imagine that the amount which would have passed beyond the limiting layer, is reflected, and added to the quantity present in the lower layers.

Scheffer[2] placed a solution underneath a volume of pure water and measured the quantity of substance which diffused upwards. The following are some of his results, n being the number of molecules of water in which one molecule of substance is dissolved.

Substance	Temperature	n	K
Hydrochloric acid	11	7·2	2·67
" "	11	108·4	1·84
Nitric acid	9	35	1·78
" "	9	426	1·73
Sulphuric acid	8	18·8	1·07
Acetic acid	13·5	84	0·77
Potash	13·6	1665	1·66
Ammonia	4·5	16	1·06
Urea	7·5	110	0·81
Mannite	10	220	0·38

[1] *Wien. Akad. Ber.*, 1879, 79, p. 161.

[2] *Ber.*, 1882–3, 15, p. 788, 16, p. 1903, and *Zeits. f. physikal. Chemie*, 1888, 2, p. 390.

In general the diffusion constant was found to be independent of variations in the concentration, but in the case of hydrochloric acid it appeared to increase somewhat as the concentration got greater.

Graham[1] and Voigtländer[2] found that the rate of diffusion in solid agar-agar jelly solutions was practically the same as in water, and as the use of these entirely gets rid of all disturbing effects due to shaking or convection currents, they have been extensively employed. Voigtländer gives the following for a 0·72 per cent. solution of sulphuric acid diffusing into a cylinder of agar jelly, a representing the number of milligrams of sulphuric acid diffusing through a given area. The results confirm Stefan's formula.

Time in minutes	a	$a\sqrt{\frac{60}{t}}$
5	0·30	1·04
60	1·08	1·08
480	3·10	1·09
2880	7·05	1·02

The distance to which a determinate concentration reaches is also proportional to the square root of the time of diffusion. Thus the formula can be tested and the constants determined, by tracing the decolorisation of a dilute alkaline solution coloured red by phenolphthallein as the acid diffuses upward. The following table, due to Voigtländer, gives the value of the diffusion constant at

[1] *Phil. Trans.*, 1861, p. 183.

[2] *Zeits. für physikal. Chemie*, 1889, 3, p. 316.

0°, 20° and 40°, and, in the last two columns, the mean temperature coefficients from 0° to 20° and 20° to 40°.

Substance	D_0	D_{20}	D_{40}	a_1	a_2
Formic acid	0·472	0·867	1·49	·0228	·0306
Acetic ,,	0·318	0·64	1·04	·0245	·0326
Propionic acid	0·245	0·514	0·882	·0261	·0358
Sulphuric ,,	0·637	1·21	2·01	·0236	·033
Hydrochloric acid	1·07	2·06	—	·0246	—
Nitric acid	1·10	2·10	—	·0226	—
Potash	1·01	1·75	2·36	·0209	·026
Soda	0·764	1·26	1·35	·0195	·024
Potassium chloride	0·786	1·40	2·18	·0219	·0279
Sodium chloride	0·535	1·04	1·71	·0243	·0332
Calcium ,,	0·394	—	1·40	—	—
Barium ,,	0·525	0·98	1·58	·0232	·0306

24. Dialysis. Graham observed that substances like tannin, albumen and gums diffused very slowly through water. He called such bodies *colloids*, and acids, salts, &c. *crystalloids*. Membranes of bladder or parchment paper allow crystalloids to pass through them, but are impermeable, or only very slowly permeable to colloids. By this process, which is called *dialysis*, a mixture of colloids and crystalloids can be separated. The results however depend on the nature of the membrane. The phenomena can perhaps be explained by the fact that colloids all possess complicated molecules which may be too large to pass through the pores of the membrane.

CHAPTER V.

FREEZING POINTS OF SOLUTIONS.

25. Historical. It has long been known that the freezing point of a salt solution, such as sea water, is lower than that of the water when pure, and in 1788 Blagden[1] published some observations on the subject, which shewed that the depression of the freezing point produced by dissolving a substance in water, was approximately proportional to the quantity of substance in solution, except when the concentration became considerable.

Further observations were made by Rüdorff[2] and Coppet[3]. The latter noticed that if the lowering of the freezing point produced by chemically equivalent quantities of different salts was examined, it was found that the molecular lowering was nearly equal for salts of similar chemical constitution.

[1] *Phil. Trans.*, 78, p. 277.
[2] *Pogg. Ann.*, 1861, 114 *et seq.*
[3] *Ann. Chim. Phys.*, 1871, 2. 23, 25, 26.

The whole subject has been fully examined by Raoult[1], who extended his observations to non-electrolytes, such as solutions in pure benzene, and solutions of organic compounds in water. He found that the depressions produced by equi-molecular quantities of different substances were nearly of the same value.

26. Connection with Osmotic Pressure and other Theoretical Considerations. Before examining the results of these experiments in detail, we will shew how the phenomena are connected with those of osmotic pressure.

It has already been noticed that the ice which freezes out from a salt solution is the ice of pure water. Since this is so, the molecules of dissolved substance, which all remain in solution, are compressed into a smaller space, and hence work has to be done in overcoming the osmotic pressure which tends to increase the volume.

Let us suppose that we have a solvent whose freezing point is T on the absolute scale of temperature, and whose latent heat is λ. Let some substance be dissolved in a large volume of it, and let the freezing point of the solution be $T - \delta T$.

Let us force out one gram of the solvent through a semipermeable membrane at a temperature of $T°$. If we neglect any difference in volume between the water when pure and when in the solution, the quantity of work done will be pv, where p = the osmotic pressure and v the volume of the solvent forced out. Then let us abstract a

[1] *Compt. rend.*, 1882, 94, p. 1517, 95, pp. 188, 1030. *Ann. Chim. Phys.*, (6), 2, p. 66, (5), 28, p. 137, (6), 4, p. 401.

quantity of heat λ (= latent heat), and so freeze the gram of solvent. If we then cool the system to $T - \delta T$, bring the ice and solution together, again thaw the ice (the water from which will do no external work in mixing with the solution), and heat to T, we shall have performed a complete cycle, and can apply the usual thermodynamic relation, that the ratio of the work done to the heat absorbed, is the same as the ratio of the difference in temperature to the absolute temperature of the system at its hottest.

$$\therefore \frac{pv}{\lambda} = \frac{\delta T}{T},$$

$$\therefore \delta T = T\frac{pv}{\lambda} \quad \text{.....(11).}$$

Let us take the case of a water solution of any body containing one gram-molecule per litre. We have seen (p. 39) that the osmotic pressure is the same as the dissolved molecules would exert in the gaseous state. It is therefore 22·32 atmospheres, or $22{\cdot}32 \times 76 \times 13{\cdot}6 \times 981$ C.G.S. units. v, the change in volume of the solution when 1 gram of solvent is frozen, is $\frac{1}{\rho}$, where ρ is the density, which gives us another form of equation (11)

$$\delta T = T\frac{p}{\lambda\rho} \quad \text{.....(12).}$$

For water $\rho = 1$, $T = 273$ and $\lambda = 79{\cdot}4$ calories or $79{\cdot}4 \times 4{\cdot}2 \times 10^7$ ergs or C.G.S. units of energy. If we calculate δT with these numbers we find that the freezing point of water should be lowered by one gram-molecule of dissolved substance per litre, by

$$1°{\cdot}86\ \text{C.}$$

Raoult[1] made many experiments on this subject and his results give a mean value of

$$1°{\cdot}85\ \text{C.}$$

for the same effect.

It is easier to make a comparison with Raoult's results by changing the form of our equation, but the effects of dissolved bodies on any solvent can be calculated from (12) by using the values for T and λ given on p. 59. This is the simplest expression of Van 't Hoff's theory, and the one which shews most clearly the connection between the lowering of freezing point and the osmotic pressure; another form however may be useful.

In our equation (11) let us put, since dilute solutions obey Boyle's law,

$$pv = RT.$$

The expression then becomes

$$\delta T = \frac{RT^2}{\lambda} \qquad \text{.....(13).}$$

R is a constant whose value for one gram-molecule of any gas or substance in dilute solution is, as we have shewn on p. 40,

$$R = \frac{pv}{T} = 8{\cdot}29 \times 10^7 \text{ ergs},$$
$$= 1{\cdot}976 \text{ calories},$$

taking Griffith's value for the mechanical equivalent of heat $J = 4{\cdot}194 \times 10^7$.

The latent heat of that quantity of solvent in which one gram-molecule is dissolved is

$$L = \lambda \frac{1000\rho}{n},$$

[1] *Compt. rend.*, 1882, 94, p. 1517.

where n represents the number of gram-molecules per litre. We then get

$$\delta T = \frac{1{\cdot}976\,T^2}{L},$$

$$= \frac{0{\cdot}001976\,T^2 n}{\lambda\rho} \quad \ldots\ldots\ldots\ldots (14).$$

In the case of water this gives $\delta T = 1{\cdot}86°n$, and of course the value for other solvents can be deduced in a similar manner.

Raoult expressed the concentrations of his solutions in terms of the number of gram-molecular weights of substance dissolved in 100 grams of the solvent. From observations on more dilute solutions, on the assumption that the law of proportionality was still applicable, he calculated the depression of the freezing point which would be produced by one gram-molecule dissolved in 100 grams of solvent.

We can at once throw our equation (14) into a form in which comparison with Raoult's results for different solvents is easy. The volume of 100 grams of solvent is $\frac{100}{\rho}$. We have seen that if we dissolve one gram-molecule in one litre of *solution*, we get an osmotic pressure of 22·3 atmospheres. If, as a first approximation, we assume that the density of the solution is the same as that of the solvent, when we dissolve the same amount in $\frac{100}{\rho}$ c.c., we get a pressure which is greater than that given by one gram-molecule per litre in the ratio of

$$1000 : \frac{100}{\rho} \text{ or } 10\rho : 1.$$

The value of R becomes 10ρ times greater than before and equation (14) assumes the form

$$\delta T = \frac{0{\cdot}00197\,T^2}{\lambda\rho} \times 10\rho = \frac{1{\cdot}97\,T^2}{100\,\lambda} \approx \frac{2T^2}{100\,\lambda} \quad \ldots(15).$$

The comparison between the values calculated from this equation by Van 't Hoff, and Raoult's observed numbers is given below.

	T	λ	$\frac{2T^2}{100\lambda}$	δT (observed)
Water	273°	79	18·9	18·5
Acetic acid	290	43·2	38·8	38·6
Formic acid	281·5	55·6	28·4	27·7
Benzene	277·9	29·1	53·0	50·0
Nitrobenzene	278·3	22·3	69·5	70·7

The agreement between these results is sufficient to shew that, at all events in dilute solutions, the theory of Van 't Hoff, which considers the osmotic pressure to be the same in its nature as gaseous pressure, leads to results which agree with observation to a considerable degree of accuracy.

Raoult stated that one molecule of a substance dissolved in 100 molecules of solvent always gave a depression of the freezing point which was approximately equal to 0·63, and supported this generalization by experiments on solutions in formic acid, acetic acid and benzene. Our theory gives no theoretical ground for such an assertion, but if we work out formula (15) for these

particular cases, we shall find that, as a matter of fact, the numbers all happen to be nearly what Raoult gave.

If the molecular weight of the solvent be M, the quantity represented by 100 gram-molecules is M times that represented by 100 grams, so that the solutions will be only $\frac{1}{M}$ as strong as those we dealt with in the last table. The new depression of the freezing point will therefore be not $\frac{2T^2}{100\lambda}$ but $\frac{2T^2}{100\lambda M}$. If we divide the figures given in the table by the molecular weights of the solvents we get for the depressions

Formic acid = 0·62.
Acetic acid = 0·65.
Benzene = 0·68.

The approximate constancy of these numbers is however a pure accident, and does not hold for other bodies; thus water gives 1·05. This point has been fully examined experimentally by Eykman[1], and the following

	Observed	Van 't Hoff's formula	Raoult's rule
Phenol	74	77	58·3
Naphthalene	69	69·4	79·4
p-Toluidine	51	49	66·3
Diphenylamine	88	98·6	104·8
Naphthylamine	78	102·5	88·7
Lauric acid	44	45·2	124
Palmitic acid	44	44·3	158·7

[1] *Zeits. f. physikal. Chemie*, 1889, 3, p. 203.

table shews his values of the molecular depressions as given by experiment, compared firstly with the numbers calculated from Van 't Hoff's formula, and secondly with those deduced from Raoult's empirical rule.

The numbers for lauric and palmitic acids seem quite conclusive in favour of Van 't Hoff. In Raoult's generalization he was misled by a purely accidental agreement of numbers, and he has since accepted Eykman's results and the accuracy of Van 't Hoff's formula.

27. Experimental Methods. The best apparatus for freezing point determinations was introduced by Beckmann, and is represented in fig. 4.

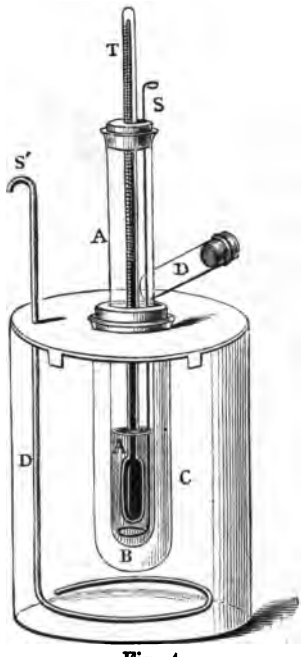


Fig. 4.

The solution to be examined is placed in a wide test-tube *A*, which is surrounded by a second larger tube *B* to serve as an air jacket. This is placed in a vessel *C*, into which a freezing mixture can be introduced. There is one stirrer in *C*, and another, made of a platinum wire, in *A*. A delicate thermometer graduated to hundredths of a degree, is also placed in *A*. It has a little reservoir at the top, into which some of the mercury

can be driven, to make the instrument available for different solvents, which freeze at different temperatures. It should be remarked however, that for accurate work the days of the mercurial thermometer are numbered, and any delicate thermometric measurement should now be made with one of Callendar's platinum thermometers, in which the temperature is determined by observing the electrical resistance of a little coil of platinum wire. The delicacy of this instrument is very great—the thousandth part of a degree being easily measured—and its use quite gets rid of irregularities due to the sticking of the mercury, which is so noticeable when working with mercurial thermometers.

The method of using Beckmann's apparatus is this. A weighed quantity of the pure solvent is introduced into *A*, and its freezing point determined by placing in *C* some mixture whose temperature is just below the point to be reached. The tube *A* is then removed, and the solvent melted. A weighed quantity of the substance to be dissolved is introduced through the side tube *D*, and the tube replaced. It is better to cool it slightly below the temperature at which it will finally stand. This can be done if it be kept quite at rest. The supercooled liquid is then stirred by means of the platinum wire, when small crystals of ice form. The temperature rises to a certain point, and then keeps stationary. If we go on freezing the solution however, it will again begin to sink, for as the solvent is frozen out, the remaining solution gets stronger, and so has a lower freezing point. The highest of these temperatures is therefore the one giving the

freezing point of the solution of the calculated concentration.

An immense number of observations have been made on this subject. The first to investigate it with any completeness was Raoult, and some of his numbers are given below. These represent what he calls the molecular depression, that is the lowering which would be produced by one gram-molecule of the substance in 100 grams of the solvent. They are calculated from observations on solutions of much less concentrations than this, on the assumption that the law of proportionality is still applicable.

Solutions in Acetic Acid.

Van 't Hoff's formula gives 38·8.

Methyl iodide	38·8	Butyric acid	37·3
Chloroform	38·6	Benzoic acid	43·0
Carbon disulphide	38·4	Water	33·0
Ethylene chloride	40·0	Methyl alcohol	35·7
Nitrobenzene	41·0	Ethyl „	36·4
Ether	39·4	Amyl „	39·4
Chloral	39·2	Glycerine	36·2
Formic acid	36·5	Phenol	36·2
Sulphur dioxide	38·5	Stannic chloride	41·3
Sulphuric acid	18·6	Magnesium acetate	18·2
Hydrochloric acid	17·2		

Solutions in Formic Acid.

Van 't Hoff's formula gives 28·4.

Chloroform	26·5	Potassium formate	28·9
Benzene	29·4	Arsenious chloride	26·6
Ether	28·2		
Aldehyde	26·1	Magnesium formate	13·9
Acetic acid	26·5		

Solutions in Benzene.

Van 't Hoff's formula gives 53·0.

Methyl iodide	50·4		
Chloroform	51·1	Methyl alcohol	25·3
Carbon disulphide	49·7	Ethyl „	28·2
Ethylene chloride	48·6	Amyl „	39·7
Nitrobenzene	48·0	Phenol	32·4
Ether	49·7	Formic acid	23·2
Chloral	50·3	Acetic „	25·3
Nitroglycerine	49·9	Benzoic „	25·4
Aniline	46·3		

Solutions in Nitrobenzene.

Van 't Hoff's formula gives 69·5.

Chloroform	69·9	Methyl alcohol	35·4
Benzene	70·6	Ethyl „	35·6
Ether	67·4	Acetic acid	36·1
Stannous chloride	71·4	Benzoic „	37·7

Solutions in Water.

Van 't Hoff's formula gives 18·9.

Methyl alcohol	17·3	Hydrochloric acid	39·1
Ethyl „	17·3	Nitric acid	35·8
Glycerine	17·1	Sulphuric acid	38·2
Cane sugar	18·5	Potash	35·3
Phenol	15·5	Soda	36·2
Formic acid	19·3	Potassium chloride	33·6
Acetic „	19·0	Sodium „	35·1
Butyric „	18·7	Calcium „	49·9
Oxalic „	22·9	Barium „	48·6
Ether	16·6	Potassium nitrate	30·8
Ammonia	19·9	Magnesium sulphate	19·2
Aniline	15·3	Copper „	18·0

An examination of these tables at once shews that the molecular depressions produced by different substances

in the same solvent are approximately constant. Leaving out of consideration for the present solutions in water, we find that in other solvents, besides a series of normal compounds, the mean of whose molecular depressions agrees with the number deduced from Van 't Hoff's theory, there is in general a series of abnormal substances which give depressions about half the others. Since on Van 't Hoff's theory the effect is proportional to the number of dissolved molecules, and independent of their nature, it is at once suggested, that, in these cases, the number of molecules is halved by aggregates of two ordinary molecules being formed, so that the molecular weight is doubled. This view is strengthened by the fact that some of the compounds which shew this effect (such for instance as the acids of the formic acid series, which give half values when dissolved in benzene or nitrobenzene) are known to form compound molecules in the gaseous state, and there is evidence from other sources (e.g. from the surface tensions) that these acids and also certain alcohols form polymeric molecules when liquid.

28. Determination of Molecular Weight. It is evident then, that the determination of the freezing point of a solution gives a means of controlling the measurement of the molecular weight of the dissolved substance. If we do not know whether the molecular weight of a body is M or nM we can see which of these values we must use in calculating the molecular depression, in order to get a number nearly equal to Raoult's mean value for the constant. It must be noticed that we can only determine

the molecular weight of a body in a certain solvent, for the same substance may have different molecular weights in different solvents (as witness the alcohols in benzene and acetic acid) and of course these *may* be all different from its molecular weight in the gaseous state, though in general one of them turns out to be the same. The nature of the solvent may affect the state of molecular aggregation, just as the conditions of temperature and pressure affect it when the substance is a gas. The solvents of the benzene series seem to favour polymerisation, while formic acid and its analogues seem generally to produce simple molecules.

In the case of aqueous solutions we again have two series, and, taken alone, we might be inclined to consider the higher numbers as normal, and to assign doubled molecular weights to those bodies which give the lower values. But when we work out Van 't Hoff's formula for the case of water, it gives, as we have seen, a value 18·9 for the molecular depression. This at once shews that the lower numbers are the normal values, and that they can be explained on Van 't Hoff's theory. It is the higher series which requires some further explanation. Are we to suppose that (as in the case of certain gases at high temperatures) dissociation occurs, and increases the number of effective pressure-producing molecules, or are we to suppose that some new cause is brought into operation? In favour of the dissociation hypothesis it may be urged that the numbers for such salts as KCl, NaCl, &c.,—which can only be dissociated into two parts, never shew values which are much greater than double the normal,

while salts such as $CaCl_2$, which can be split into three, sometimes give a molecular depression which is about three times the normal value. The fuller discussion of this hypothesis we must defer till we are considering the electrical properties of solutions, but we will here state the most important fact that all those substances which give abnormally great values for the molecular depression of the freezing point in aqueous solution, form, when dissolved in water, solutions which are electrolytes. Moreover their electrical conductivities bear a simple relation to the amount of dissociation which it is necessary to assume in order to account for the abnormal effect on the freezing point. Whatever is the cause of this abnormally great molecular depression, is certainly also the cause of electrolytic conductivity.

29. Influence of Concentration. The account of the subject of freezing points given above does not apply to strong solutions, for Van 't Hoff's theory only holds good when the dilution is so great that the effect of the forces between the molecules can be neglected. As the strength increases we get deviations from the law that the depression is proportional to the concentration. The depression coefficients of some substances increase, and of others decrease as concentration gets greater. The effect of increasing concentration on the freezing points of indifferent substances (i.e. non-electrolytes) has been studied by Beckmann[1] and Eykman[2]. They find that

[1] *Zeits. f. physikal. Chemie*, 1888, 2, p. 715.
[2] *Ibid.*, 1889, 4, p. 497.

in almost all cases the molecular depression changes nearly in proportion to the concentration, and that it more usually increases than decreases when a greater quantity of substance is dissolved. This makes the curves drawn between the concentrations as abscissæ and the molecular depressions as ordinates, nearly straight lines, inclined at a small angle with the axis of the abscissæ. In some cases the molecular depression decreases faster than the concentration increases, and, at high concentrations, may even be reduced to half its former value. If we extend our method of calculating molecular weights to such solutions, it indicates that the molecular weight has doubled at the high concentration, so that polymerisation must have occurred. These cases are few; they include such solutions as those of acetoxim and other oxims in benzene, and must be considered analogous to the case of gaseous nitrogen peroxide at moderate temperatures.

In general the change of molecular depression is far less than in these oxim solutions, and must be considered to be analogous to the variation from the usual laws shewn by gases at high pressures, rather than to a case of gaseous polymerisation. The best value for the molecular weight would obviously be obtained by producing the curve shewing the depression of the freezing point till it cut the axis of no concentration, and using this value in the calculation. It is probable that the small deviations of Raoult's numbers for non-electrolytes from the calculated values would become still smaller if this correction for concentration were applied to his observations.

The variation from their ideal laws of gases at high

pressures can be approximately expressed by Van der Waal's formula

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where the pressure p is increased by a term proportional to the molecular attraction (a) and inversely proportional to the square of the volume, and the volume v is diminished by a constant b which is equal to four times the actual volume occupied by the substance of the molecules themselves and is unaffected by any change in pressure. An equation of the same nature has been developed by Ostwald, Bredig and Noyes, taking account of the molecular volumes of the solvent and of the substance dissolved, and of the interactions between them. In general these latter are very small, and on simplification the formula reduces to

$$p(v - d) = K \quad \ldots\ldots\ldots\ldots\ldots\ldots (16),$$

where the constant d expresses a correction for volume, which depends on the nature both of the solvent and of the substance in solution. The results deduced from this equation agree well with observations made by Beckmann on acetone dissolved in benzene, and on chloral hydrate in water.

A long series of determinations of the freezing points of dilute solutions of inorganic and organic bodies dissolved in water has been made by H. C. Jones[1]. His results for organic substances shew that in general the molecular depression decreases as the concentration increases till a certain critical concentration, at which the molecular

[1] *Zeits. f. phys. Chemie*, 1893, 11, pp. 110 and 529, 12, p. 623.

depression is a minimum, is reached, after which it begins to increase again as the concentration is made still greater. This is shewn by the annexed table for cane sugar in water.

Concentration in gram-molecules per litre	Molecular depression $\delta T/n$	Concentration in gram-molecules per litre	Molecular depression $\delta T/n$
0·00234	2·35	0·117	1·94
·00467	2·36	·154	1·96
·00930	2·29	·203	2·00
·0292	2·27	·585	2·32
·0728	2·08	1·169	2·91
·0933	1·99		

The kind of variation in this case is obviously the same as in the case of air at high pressures investigated by Amagat (see Tait's *Properties of Matter* § 200) who found the following results.

Pressure in atmospheres	pv	Pressure in atmospheres	pv
1·00	1·0000	94·94	·9814
31·67	·9880	133·51	·9905
59·53	·9815	282·29	1·0837
73·03	·9804	400·05	1·1897

We see by equation (11) p. 56 that δT varies as pv, so that it is analogous to pv in the case of a gas. Thus the existence of a minimum value of the molecular depression of the freezing point, is exactly paralleled by the deviation of air from the gaseous laws.

The behaviour of very much stronger solutions has been examined by Pickering[1] who finds that in such cases great deviations from the gaseous laws occur. The following table gives the molecular depression produced by n molecules dissolved in 100 molecules of solvent.

Substance	$n=1$	5	10	50	100	300	1000	2000
Solvent = Water								
Methyl alcohol	1·05	1·05	1·05	1·03	0·825			
Ethyl „	1·10	1·06	1·15	0·815	0·548			
Acetic acid	1·04	0·944	0·865	0·52				
Solvent = Benzene								
Methyl alcohol	0·6	0·31	0·22	0·077	0·055	0·042	0·040	0·031
Ethyl „	0·6	0·33	0·22	0·10	0·076	0·067	0·044	0·038

Thus in all cases the molecular depression gets less when the concentration is increased. This is contrary to Jones' result for fairly strong solutions, but if we expressed Pickering's numbers in gram-molecules per 100 cubic centimeters of *solution*, instead of in 100 gram-molecules of *solvent*, the value of n would be less, and that of $\delta T/n$ increased, and this difference would increase as the concentration increased. The densities of mixtures of ethyl alcohol and water are known, and if we calculate the molecular depression (n = number of gram-molecules per 100 c.c. of solution) for the mixture under the column 100 we get $\delta T/n = 1{\cdot}38$ instead of 0·548, and this is greater than the value when $n = 1$ viz. 1·10.

[1] *Chem. Soc. Jour. Trans.* 1893, 63, p. 998.

The difference between the results obtained by measuring the concentration by the number of gram-molecules per litre, and measuring it by the number of gram-molecules to 1000 grams of solvent, is well shewn by the tables and diagrams given by Abegg[1], who has determined the freezing points of many concentrated solutions. A higher value for the molecular depression is always obtained by using the former method, and as the concentration increases the difference becomes very great indeed.

30. Cryohydrates. Since the solubility of a solid usually increases as the temperature rises, the solution which is just saturated at the freezing point can retain all its contents at higher temperatures. If such a solution is cooled, it again becomes saturated when the freezing point is reached, and as ice is frozen out, solid must be deposited, because there now remains insufficient solvent to keep it in solution. The ice and dissolved substance will therefore be deposited in the proportion in which they exist in solution, and since the concentration of the remaining liquid keeps unchanged, the temperature will be constant till all has solidified. The ice and salt are not deposited in combination, but only side by side, for they never form clear definite crystals, and alcohol will dissolve out the ice, leaving a framework of solid salt. Owing to the constancy in the melting points and composition of such bodies, they have been regarded by Guthrie and others as definite chemical compounds. The application of our present knowledge of the properties of solu-

[1] *Zeits. f. physikal. Chemie*, 1894, 15, p. 209.

tions however will, as shewn above, completely explain their existence, without the need of such an assumption.

31. Melting points of Alloys. If metals are dissolved in mercury, they produce depression of the melting point, just as bodies dissolved in water produce depression of the freezing point. Tammann examined solutions of potassium, sodium, thallium and zinc, and found Raoult's laws approximately true. These metals seem to form monatomic molecules.

Heycock and Neville[1] used sodium and tin as solvents, and found the following values for the atomic depressions:

Solutions in Sodium.

Gold	4·50—4·87	Cadmium	3·17—3·92
Thallium	4·27—4·73	Potassium	3·34—3·85
Mercury	4·37—4·53	Indium	3·37—3·77

Solutions in Tin.

Silver	2·93	Cadmium	2·43
Gold	2·93	Mercury	2·39
Copper	2·91	Calcium	2·40
Sodium	2·84	Indium	1·86
Magnesium	2·76	Aluminium	1·25
Lead	2·76		

Indium and Aluminium thus shew a tendency to form more complex molecules when dissolved in tin.

The chief interest of these experiments lies in their influence on our views as to the nature of alloys, which must now be considered as solutions of one metal in another.

[1] *Chem. Soc. Journ.* 1889, 1890.

CHAPTER VI.

VAPOUR PRESSURES OF SOLUTIONS.

32. Theoretical Considerations. If any non-volatile substance be dissolved in water, it will be found that the boiling point is higher than that of the pure solvent. A liquid boils when its vapour pressure is equal to the pressure of the atmosphere, and we see from the above statement that the effect of the dissolved substance is to make it necessary to heat the liquid to a higher temperature in order to reach such a pressure, that is to say, that at any given temperature the vapour pressure is reduced. This effect of decreasing the vapour pressure obeys much the same laws as those which govern the depression of the freezing point. The experimental difficulties of determining it are however much greater. Let us first examine its connection with the osmotic pressure, to which it must evidently be related, since the air over an evaporating liquid acts as a semipermeable membrane in allowing the solvent, but not the dissolved substance, to escape. A thermodynamic investigation similar to that applied on p. 55 to freezing points, was given by Van 't Hoff, but a more direct method due to Arrhenius will be reproduced here.

Suppose that a long tube, open at the top and closed below by a semipermeable membrane, is filled with the solution of some non-volatile, indifferent substance, and placed in an exhausted bell-jar with its lower end dipping in water. Water will enter or leave the apparatus till the level of solution in the tube is such that the potential energy of the system is at a minimum value, so that any further rise would involve an increase in the potential energy. We may then say that the pressure due to the column of liquid is equal to the osmotic pressure of the solution, if we understand the term osmotic pressure to include all those properties which cause the potential energy of the solution to increase when the concentration gets greater, whether they are due to the movement of the dissolved molecules, to volume changes on dilution, to chemical action between the dissolved substance and solvent, or to other causes.

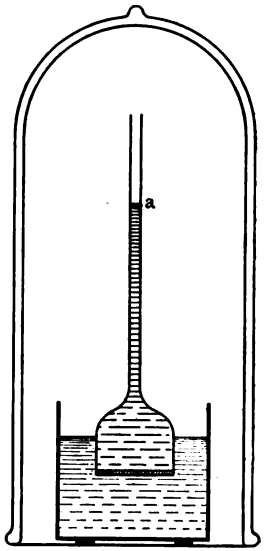


Fig. 5.

If h is the height of the column of liquid in centimetres, ρ its density, and s the density of mercury, the osmotic pressure when there is equilibrium is

$$P = \frac{10\,h\rho}{s} \text{ mm. of mercury.}$$

The bell-jar has become filled with the vapour of the

solvent, and at the level a, at which the liquid stands in the tube, the pressure of this atmosphere of vapour must be equal to the vapour pressure of the solution. If this were not so there could not be equilibrium, and vapour would continually leave the solution at a, or condense there; water would at the same time enter or leave through the membrane to compensate for this process, and a continuous, automatic circulation would be set up. Since by the principles of thermodynamics we know this to be impossible, the vapour pressure of the solution must be less than that at the surface of the pure solvent by the pressure due to a column of vapour of height h. If, for a first approximation, we assume that the density of the vapour is uniform throughout that column we get

$$\pi' = \pi - \frac{10\,h\sigma}{s},$$

where π represents the vapour pressure of the solvent, π' that of the solution, and σ the density of the vapour.

But $$h = \frac{Ps}{10\rho},$$

$$\therefore\ \pi' = \pi - \frac{P\sigma}{\rho} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (17),$$

so that the lowering of the vapour pressure is $P\sigma/\rho$, or the osmotic pressure multiplied by the density of the vapour under its existing pressure and divided by that of the solution.

The density of the vapour may be considered to be proportional to the pressure, and for very dilute solutions, when the column h is short, we may treat the pressure as

everywhere equal to π. If the density of the vapour at 760 mm. is σ_0 we have

$$\sigma = \sigma_0 \frac{\pi}{760}.$$

The density of the vapour will also be inversely proportional to the absolute temperature, but since the osmotic pressure P is directly proportional to the same thing, the correction goes out, and our result will be independent of temperature.

We thus get

$$\pi - \pi' = \frac{P\sigma}{\rho} = \frac{P\sigma_0\pi}{760\rho},$$

$$\therefore \frac{\pi - \pi'}{\pi} = \frac{P\sigma_0}{760\rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots (18),$$

which gives us the ratio of the decrease in the vapour pressure, to the vapour pressure of the solvent.

Let us take the case of one gram-equivalent of some indifferent substance dissolved in water, in such a way that the volume of the solution is one litre. This, as we have seen, gives an osmotic pressure equal to 22·3 atmospheres or

$$22{\cdot}3 \times 760 \text{ mm. of mercury,}$$

d_0, the density of water vapour at normal temperature and pressure is 9/11160, and ρ, the density of the solution when it is dilute, can be put equal to that of water, viz. unity. Thus we get

$$\frac{\pi - \pi'}{\pi} = \frac{22{\cdot}3 \times 760 \times 9}{760 \times 11160} = 0{\cdot}0180.$$

Raoult determined the decrease of vapour pressure of water caused by the solution of various bodies in it. He found that if different bodies were dissolved in the pro-

portion of their molecular weights, the lowering of vapour pressure was the same for all. For a strength of solution represented by 1 molecule in 100 molecules of solvent he found that the mean value of the ratio of the decrease of pressure to the whole pressure, when water was the solvent and indifferent bodies were dissolved, was 0·0102. If instead of this strength, we have one gram-molecule in one litre of solution or (which is the same thing for very dilute solutions) one litre (that is 1000 grams) of water, we have reduced the mass of solvent in the ratio of $18 \times 100 : 1000$ (since 18 is the molecular weight of water) and so increased the concentration in the ratio of 10 : 18. The result of Raoult's experiments then is to shew that in a dilute solution containing one gram-molecule per litre the relative lowering of the vapour pressure is

$$0{\cdot}0102 \times 1{\cdot}8 = 0{\cdot}0184,$$

a number almost identical with that deduced from the osmotic pressure.

This expression has been obtained by assuming that the density of the vapour in our exhausted bell-jar (see p. 75) is everywhere uniform. Such an assumption is only justified if the column of vapour of height h is very short, that is if the osmotic pressure, and therefore the concentration of the solution, is exceedingly small. Where this is not the case we must divide the height of vapour h into a number of parts each equal to dh and put

$$d\pi = \frac{10}{s}\sigma \,.\, dh,$$

$$\therefore\ d\pi = \frac{10}{s} \cdot \frac{\sigma_0 \pi}{760} \,.\, dh,$$

$$\therefore dh = \frac{s}{10} \cdot \frac{760}{\sigma_0} \cdot \frac{d\pi}{\pi}.$$

By integrating from 0 to h we get

$$h = \frac{760\, s}{10\sigma_0} \log_e \left(\frac{\pi_0}{\pi_h}\right),$$

π_0 being the pressure at the level of the water, *i.e.* the vapour pressure of the pure solvent, and π_h the pressure at the height h, *i.e.* the vapour pressure of the solution.

Now
$$h = \frac{Ps}{10\rho},$$

$$\therefore \log_e \left(\frac{\pi}{\pi'}\right) = \frac{P\sigma_0}{760\rho} \quad \ldots\ldots\ldots\ldots\ldots (19).$$

This equation gives a necessary relation between the osmotic pressure and the lowering of the vapour pressure of any solution, and is quite independent of the view we take as to the real cause of osmotic pressure. Whatever the cause of it may be, we know that osmotic pressure exists, and it therefore follows that the vapour pressure must be lowered by the amount shewn in our equation. The value of the osmotic pressure can thus be deduced from observations on the diminution of the vapour pressure, just as it can from observations on the lowering of the freezing point.

It is easy to transform our equation into a form which gives the concentration of the solution in terms of the ratio of the number of molecules of dissolved substance to the number of molecules of solvent, which was Raoult's method. The osmotic pressure P is $22{\cdot}32 \times 760$ mm. of mercury for a strength of 1 gram-equivalent in 1000 c.c.,

and so for a strength of n gram-equivalents in V c.c. its value is

$$P = \frac{22{\cdot}32 \times 760}{\frac{1}{1000}} \times \frac{n}{V}.$$

Now the mass of the solvent is NM, where N is the number of gram-molecules and M its molecular weight, and the volume is the mass divided by the density

or
$$V = \frac{MN}{\rho},$$

$$\therefore\ P = \frac{22{\cdot}32 \times 760 \times 1000 \times n\rho}{NM},$$

σ_0 the density of the vapour under normal conditions of temperature and pressure is

$$\sigma_0 = \frac{M}{22{\cdot}32 \times 1000},$$

assuming that the molecular weight of the vapour has the same value as we have taken for it in the liquid condition.

We thus get by substituting in equation (18)—

$$\frac{\pi - \pi'}{\pi} = \frac{n}{N}.$$

If we treat equation (19), which gives the strict relation with the osmotic pressure, in the same way, assuming as before that P is proportional to the concentration, we get

$$\log_e\left(\frac{\pi}{\pi'}\right) = \frac{n}{N}.$$

Now $\log_e\left(\frac{\pi}{\pi'}\right)$ can be written as

$$\log_e\left\{1 + \left(\frac{\pi - \pi'}{\pi'}\right)\right\},$$

and since $\pi - \pi'$ is small compared with π' this may be developed in a series

$$\frac{\pi - \pi'}{\pi'} - \tfrac{1}{2}\left(\frac{\pi - \pi'}{\pi'}\right)^2 + \ldots\ldots$$

All except the first term will be small, so that we may put as a fair approximation—

$$\frac{\pi - \pi'}{\pi'} = \frac{n}{N},$$

$$\therefore \frac{\pi'}{\pi - \pi'} = \frac{N}{n},$$

adding 1 to each side

$$\frac{\pi}{\pi - \pi'} = \frac{N+n}{n},$$

$$\therefore \frac{\pi - \pi'}{\pi} = \frac{n}{N+n} \ldots\ldots\ldots\ldots (20),$$

which is the exact expression deduced empirically by Raoult from the results of his experiments.

But this result, unlike our equation (19) on p. 79, has been deduced by making an assumption which is only true for dilute solutions, namely that the osmotic pressure is proportional to the concentration. It therefore gives results which fail to represent the truth when the concentration becomes considerable.

Thus for solutions of turpentine in ether

$\frac{p}{N}$	·0627	·1377	·3055	·5504	·9194	1·817,
$\log_e\left(\frac{\pi}{\pi'}\right)$	·0619	·1278	·2473	·391	·576	·865.

For dilute solutions however it gives good results and has a great advantage over the other equation, inasmuch as it shews that if solutions be prepared which contain the same

number of molecules of dissolved substance in the same number of molecules of *solution*, the relative lowering of the vapour pressure will be the same for all.

Thus if we have solutions in each of which there is one molecule dissolved in 100 molecules of *solvent*, that is in 101 molecules of solution,

$$\frac{\pi - \pi'}{\pi} = \frac{1}{101} = 0{\cdot}0099.$$

Raoult first shewed that if the same number of gram-molecules of various indifferent substances were dissolved in water, or other solvents, the relative lowering of the vapour pressure was very nearly constant. He then took twelve solvents and, dissolving many bodies in each, proved that for a strength of solution of 1 molecule in 100 molecules the relative lowering of pressure was nearly constant and equal to 0·0104.

In 1890 however he shewed[1] that when acetic acid was used as a solvent, the number obtained was 0·0163. This seems not to agree with the results of our equations, but in deducing them it must be remembered that (on p. 80) we assumed that the molecular weight of the vapour was the same as that which we took for the liquid. Now in preparing the solution the normal value of the molecular weight was of course assumed for the liquid, and it is known that at moderate temperatures the vapour density of acetic acid is abnormal, shewing that its molecular weight is also abnormal. At the boiling point 118° C., the ratio of the actual to the theoretical vapour density

[1] Raoult and Recoura, *Compt. Rend.* 1890, 110, p. 402.

is 1·64, which makes our theoretical number 0·0162. This indicates that we must always correct our theoretical number in this way by multiplying it by the ratio of the actual to the theoretical vapour density. Raoult gave the following numbers for six solvents—

Solvent	Temperature	$\frac{n}{N+n}$ (corrected for vapour density)	$\frac{\pi-\pi'}{\pi}$ (observed)
Water	100	0·0102	0·0102
Ethyl alcohol	78	0·0101	0·0101
Ether	20	0·0103	0·0104
Carbon bisulphide	24	0·0100	0·0099
Benzene	80	0·0101	0·0101
Acetic acid	118	0·0162	0·0163

Thus, as in the case of the depression of the freezing point, we have a satisfactory theory of the lowering of vapour pressure for the case of dilute solutions. For stronger solutions variations appear, as we observed in the case of freezing points. There is a simple method of connecting the two effects, which are evidently related since we have deduced both of them from the osmotic pressure.

Suppose we have lowered the temperature of some pure water to its freezing point, and allowed ice to separate. The ice is in equilibrium with the liquid, and unless heat be added to or taken away from the mixture, there is no tendency for the quantity of ice to increase or diminish. It follows that the ice and the water at the freezing point must have the same vapour pressure, otherwise if we had

ice and water in a closed vessel, vapour would pass away from the body with the higher pressure, and condense on that which had the lower pressure, and the quantity of ice would increase or diminish. By the same reasoning we can shew that at the freezing point of a solution, when it can exist in equilibrium with ice, its vapour pressure must equal that of the ice. If then we know how the vapour pressure of ice varies with the temperature, we can find what decrease of temperature is necessary to reduce the vapour pressure by the same amount as the dissolved substance decreases that of the water, and this gives the lowering of the freezing point.

This shews that whatever the variations in the lowering of the freezing point at great concentrations, there must be a corresponding variation in the diminution of vapour pressure at the freezing point which can at once be calculated, but as most of the observations on vapour pressures have been made at higher temperatures, various approximate assumptions have to be made in order to correlate the two series of results.

The following investigation of this connection is taken from Ostwald's *Lehrbuch*.

The relation between the quantity of heat λ_0 required to evaporate unit mass of liquid, the vapour pressure π_0, and the volume of the saturated vapour V, is as we have seen on p. 26—

$$\frac{\lambda_0}{T} = \frac{d\pi_0}{dT} V.$$

But $$V = \frac{RT}{\pi_0}, \qquad \therefore \frac{\lambda_0}{RT^2} = \frac{1}{\pi_0}\frac{d\pi_0}{dT} = \frac{d}{dT}\log_e \pi_0.$$

A similar expression holds good for ice, but in this case the heat of evaporation, λ_1, is greater, for the heat required to melt the ice must be added to that required to vaporise the water.

$$\therefore \frac{\lambda_1}{RT^2} = \frac{d}{dT} \log \pi_1,$$

where p_1 is the vapour pressure of ice; the difference is

$$\frac{\lambda_1 - \lambda_0}{RT^2} = \frac{d}{dT}\left(\log \frac{\pi_1}{\pi_0}\right).$$

But $\lambda_1 - \lambda_0$ is the heat of fusion of ice, which has the value $(79{\cdot}04 + {\cdot}49t)$, t denoting the temperature in degrees from the Centigrade zero.

$$\therefore d \log \frac{\pi_1}{\pi_0} = \frac{(79{\cdot}04 + {\cdot}49t)}{RT^2} dT.$$

Taking the value of R which corresponds to one gram of water (viz. 2/18 calories per degree, see p. 41), treating T^2 as constant in the denominator, and neglecting t^2 we get

$$\log \frac{\pi_1}{\pi_0} = {\cdot}00954t.$$

33. Boiling Points. It is more convenient in some cases to measure the boiling point of a solution than its vapour pressure at some other temperature. Since the effect of the dissolved substance is to reduce the vapour pressure at any given temperature, it must raise the boiling point, and the relation between the two is easily found. Let ΠΠ be a portion of the vapour pressure curve of a solvent and Π′Π′ a portion of that of a solution. If the solution is dilute, so that the change in the vapour pressure is small, we may consider the part of the curve for the pure solvent that we want to use to be a straight

line. Any vertical line cutting ΠΠ in A and Π′Π′ in B will represent the change in vapour pressure at a certain temperature, and CB drawn horizontally from the point B to cut ΠΠ in C, will represent the change in boiling point, δT.

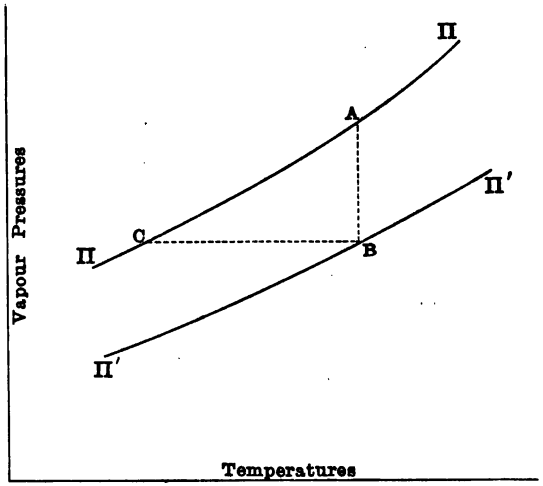


Fig. 6.

Now whatever be the direction and form of the solution curve Π′Π′, $AB = CB \tan ACB$,

$$\therefore \pi - \pi' = \delta T \tan ACB$$

$$= \delta T . \frac{d\pi}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (21).$$

If we observe δT and know $d\pi/dT$ for the pure solvent, we can at once calculate $\pi - \pi'$. The value of $d\pi/dT$ can be experimentally determined by measuring the boiling point of the solvent first when the barometer is high and then when it is low, and dividing the difference in pressure by the difference in temperature.

Another method of getting $d\pi/dT$ is to use Clausius' equation which we deduced from the principles of thermodynamics on p. 26 and used on p. 84.

$$\frac{d\pi}{dT} = \frac{\lambda}{(V-v)\,T},$$

where λ = latent heat, V the volume of the saturated vapour and v the volume of the liquid. If we assume that the vapour obeys the gaseous law $\pi V = RT$, we get, since v is small,

$$\frac{d\pi}{dT} = \frac{\lambda\pi}{RT^2},$$

$$\therefore \pi - \pi' = \delta T \frac{\lambda\pi}{RT^2}$$

or

$$\frac{\pi - \pi'}{\pi} = \delta T \frac{\lambda}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (22).$$

Now for 1 gram-molecule of the vapour the value of R is 1·974 calories: calling this 2 we can put

$$\frac{\pi - \pi'}{\pi} = \delta T \frac{\lambda}{2T^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (23).$$

From this expression the relative lowering of vapour pressure can be calculated from observations on the rise of boiling point.

In order to examine the validity of our theory, let us calculate δT for special cases. Raoult, assuming that the law of proportionality still held, found that for a strength of solution of 1 molecule in 100 molecules of solvent $(\pi - \pi')/\pi$ was equal to ·01 (see p. 82), so that for this concentration our equation gives

$$\delta T = \frac{\cdot 02 T^2}{\lambda}.$$

The following table gives the calculated values of $\cdot 02T^2/\lambda$ and the mean results for the molecular rise of boiling point, deduced from observations on very dilute solutions in different solvents by Beckmann's method.

Solvent	δT (observed)	$\frac{\cdot 02T^2}{\lambda}$ (calculated)
Water	4 to 5	5·2
Alcohol	10 to 12	11·5
Acetone	17 to 18	16·7
Ether	21 to 22	21·1
Carbon bisulphide	22 to 24	23·7
Acetic acid	25	25·3
Ethyl acetate	25 to 26	26·0
Benzene	25 to 27	26·7
Chloroform	35 to 36	36·6

34. Experimental Methods. Determinations of the vapour pressures of solutions have been made by Faraday, Wüllner, Tammann, Emden, Raoult, Walker, Beckmann, and others. Raoult[1] was the first to examine solutions of indifferent substances, and to use solvents other than water. His method consisted in comparing the heights of three mercurial barometric columns, the space over one being empty, and the others containing the vapours from the pure solvent and from the solution respectively. The depressions of these columns as compared with the first gave the vapour pressure of the solvent and of the solution. Raoult found that

[1] *Compt. Rend.* 1886–7, 103, p. 1125; 104, p. 1430.

(i) The relative lowering of the vapour pressure $(\pi - \pi')/\pi$ is independent of temperature.

(ii) For dilute solutions $(\pi - \pi')/\pi$ is proportional to concentration, but as the solutions get stronger it is more nearly represented by $n/(N+n)$, where n and N are the numbers of molecules of dissolved substance and of solvent respectively.

(iii) The molecular lowering of vapour pressure (i.e. the lowering produced by 1 gram-molecule in 100 grams of solvent) is independent of the nature of the dissolved substance. Thus for ethereal solutions he found

	Molecular weight	Molecular lowering
Carbon hexachloride	237	·71
Turpentine	136	·71
Cyanic acid	43	·70
Benzaldehyde	106	·72
Aniline	43	·71
Antimony chloride	228·5	·67

(iv) When the ratio of the number of molecules of the dissolved substance to the number of molecules of the solvent is made the same, the lowering of vapour pressure is independent of the nature of the substance and of the solvent. (For table see p. 83.)

We have already seen that all these laws can be deduced from the theory of dilute solutions. Stronger solutions shew deviations in their vapour pressures as in their osmotic pressures and freezing points, under which latter heading the influence of increasing concentration has been discussed from the point of view of the theory.

There are several objections to the barometric method. The quantity of vapour is so small that any more volatile impurity in the liquid would produce a large error, and since evaporation only occurs at the surface, the upper layers of the solution get stronger and give too small a vapour pressure. Beckmann[1] improved the method by allowing the solution to evaporate into a small flask. He then calculated the quantity of vapour produced from the decrease in weight of the solution, which was contained in a weighed bulb.

A method applicable to low temperatures has been introduced by Ostwald and Walker[2]. A current of air is passed through two bulbs containing the solution, and is thus saturated with its vapour. It is then led through another bulb containing pure water. Since this gives a higher vapour pressure, the air takes up more water and again becomes saturated. Finally the whole of the aqueous vapour is extracted by passing the air through pumice moistened with sulphuric acid. The gain in weight of the sulphuric acid gives the whole quantity of vapour evaporated, and the loss in weight of the water bulb gives the difference between that furnished by it and that furnished by the solution. Thus the ratio $(\pi - \pi')/\pi$ is at once found.

Beckmann has also used the boiling point method. It is necessary to measure the temperature of the solution, and not the temperature of its vapour which is the same as that of the pure solvent. To prevent "bumping" a

[1] *Zeits. f. phys. Chemie*, 1889, 4, p. 532.
[2] *Ibid.*, 1888, 2, p. 602.

piece of platinum wire is sealed through the bottom of the flask. Boiling then takes place exclusively from the end of this, and a constant and uniform stream of bubbles is given off.

Tammann[1] has measured vapour pressures at 100° by noticing what decrease of external pressure was required to make the liquid boil at that temperature. He gives an immense number of figures shewing the diminution of vapour pressure in millimetres of mercury, due to the solution of n gram-molecules in 1000 grams of water. We select a few of them to which we shall have occasion to refer.

	$n=0{\cdot}5$	1	2	3	4	5	6
Potassium chloride	12·2	24·4	48·8	74·1	100·9	128·5	152·2
Sodium "	12·3	25·2	52·1	80·0	111·0	143·0	176·5
Potash (KOH)	15·0	29·5	64·0	99·2	140·0	181·8	223·0
Aluminium chloride	22·5	61·0	179·0	318·0			
Calcium "	17·0	39·8	95·3	166·6	241·5	319·5	
Barium "	16·4	36·7	77·6				
Succinic acid	6·2	12·4	24·8	36·7	48·5	59·7	71·2
Citric "	7·9	15·0	31·8	50·0	71·1	92·8	
Lactic "	6·5	12·4	24·0	34·3	44·7	55·0	65·6

If we calculate the theoretical depression for a concentration of 0·5 gram-molecule in 1000 grams of water from equation (20) on p. 81

$$\frac{\pi - \pi'}{\pi} = \frac{n}{N+n}$$

we get $\pi - \pi' = 760 \times \dfrac{0{\cdot}5}{\frac{1000}{18} + 0{\cdot}5} = 6{\cdot}8$ mm. of mercury.

[1] *Mém. Acad. Pétersb.*, 1887, 35, No. 9. Table in Ostwald's *Lehrbuch.*

Thus we see that bodies like lactic and succinic acids give a result which agrees well with theory, while metallic salts are abnormal. Salts like potassium chloride, KCl, give numbers nearly double the figure deduced from theory, calcium and barium chlorides, $CaCl_2$ and $BaCl_2$, produce nearly three times, and aluminium chloride, $AlCl_3$, nearly four times the normal effect.

As in the case of the depression of the freezing points, these exceptions to the usual law are all electrolytes. It is also important to note that KCl contains two atoms, $CaCl_2$ three atoms and $AlCl_3$ four atoms. The lowering of the vapour pressure by electrolytes seems then to be proportional to the number of atoms in the molecule. The discussion of these relations must be postponed for the present.

35. Influence of Concentration. Tammann's results shew that in general the lowering of vapour pressure increases faster than the concentration for metallic salts, but appears to be nearly proportional to it for indifferent substances. The concentration of Tammann's solutions is expressed in terms of the number of gram-molecular weights of salt dissolved in 1000 grams of *water*. If we convert it into the number of gram-molecules in a litre of *solution*, the result will be to make the molecular lowering of vapour pressure increase faster as the concentration gets greater (see p. 71).

36. Determination of Molecular Weights. Like the depression of the freezing point, the lowering of vapour pressure has been used to determine the molecular

weight of bodies in solution. It can be used for high temperatures, and for cases (such as for solutions in alcohol) when the freezing point method is not applicable. In this way Beckmann obtained the molecular weights of iodine, phosphorus and sulphur in solution. It was found that 1·065 grams of iodine, dissolved in 30·14 grams of ether, raised the boiling point by 0·296°. This concentration corresponds to $(1{\cdot}065 \times 7400)/(30{\cdot}14 \times M)$ gram-molecules of iodine in 7400 grams (100 gram-molecules) of ether. Now it can be proved either by experimenting with a body of known molecular weight, or by calculation from our formulæ, that 1 gram-molecule of any indifferent substance, dissolved in 100 gram-molecules of ether, gives a change in the boiling point of 0·284°. The above strength of solution must therefore be 296/284 gram-molecules.

$$\therefore \frac{1{\cdot}065 \times 7400}{30{\cdot}14\, M} = \frac{296}{284},$$

$$\therefore M = 250{\cdot}3.$$

The atomic weight of iodine is 127, so that in ethereal solution the molecule consists of two atoms.

In a similar manner it was shewn that the molecule of phosphorus in carbon bisulphide contains 4 atoms, as it also does in the state of vapour, but that in the same solvent the molecule of sulphur consists of 8 atoms, whereas the vapour density gives a formula S_6.

The vapour pressures of amalgams have been examined by Ramsay[1] who found that in nearly all cases the lowering of vapour pressure corresponded to that

[1] *Chem. Soc. Journal Trans.*, 1889, p. 521.

which would be produced by monatomic molecules. The value deduced for the molecular weight of potassium however is less than its atomic weight (29·6 instead of 39·1) and the numbers for calcium and barium (19·1 and 75·7) correspond to half their atomic weights. What this means it is as yet impossible to say. Aluminium and antimony tend to form more complex molecules.

37. Solutions of Gases in Liquids. We have already seen (p. 10) that, with reference to their solubility in liquids, gases can be divided into two classes: firstly those which are completely removed by boiling the liquid or decreasing the pressure, and secondly those which cannot be so removed.

In the first case, where the dissolved gas obeys Henry's law that the mass dissolved is proportional to the pressure, the laws of the vapour pressure are very simple. Let us consider the case of a mass of air saturated with water vapour over a saturated solution of air in water. We know that if the external pressure be reduced, some air will at once come out of solution, while if the pressure be increased more goes in. If we have then some water with air dissolved in it over the mercury in a barometer tube, air will be expelled till its pressure in the barometric vacuum is equal to the pressure of that dissolved, and whatever changes may occur in order that there may be equilibrium, the water must always keep saturated with air under the existing conditions of temperature and pressure. The pressure of aqueous vapour from the solution will obey

the usual laws, and will therefore be less than that from pure water in accordance with our equation

$$\frac{\pi - \pi'}{\pi} = \frac{n}{N+n},$$

or

$$\pi' = \pi\left(1 - \frac{n}{N+n}\right),$$

for the air in solution will exert osmotic pressure just like other substances. The total vapour pressure of the solution will be the sum of this and of the pressure due to the air, which, as we have seen, equals that in the vacuous space. This latter will depend on the relative volume of the solution and of the vacuous space, which takes air from the solution till there is equilibrium, so the measured vapour pressure would depend on the dimensions of the apparatus. We can however calculate the total vapour pressure in any given case if we know the concentration of the solution. Thus if there are n gram-molecules of gas dissolved in N gram-molecules of solvent, the diminution of the pressure of aqueous vapour (due to osmotic pressure) is

$$\pi - \pi' = \pi \frac{n}{N+n},$$

or for dilute solutions

$$\pi - \pi' = \pi \frac{n}{N}.$$

If we know λ_0 the solubility of the gas at 760 mm. pressure and 0° C., we can find the vapour pressure of the dissolved gas, for

$$\lambda_0 = \frac{v_0}{V},$$

where v_0 is the volume of gas dissolved under normal conditions and V the volume of the solution.

In a volume v_0 c.c. there are $v_0/22320$ gram-molecules. Let us call this number n_0, then by Henry's law

$$\frac{n}{n_0} = \frac{p}{760},$$

where p is the pressure of gas.

$$\therefore p = 760\,\frac{n}{n_0} = \frac{760 \times 22320\, n}{\lambda_0 V}.$$

V, the volume of the solvent, contains $\frac{V\rho}{M}$ gram-molecules, where M = molecular weight and ρ the density of the solvent,

$$\therefore V = \frac{MN}{\rho},$$

$$\therefore p = \frac{760 \times 22320\,\rho}{\lambda_0 M} \cdot \frac{n}{N}.$$

This gives the increase in the total vapour pressure due to the gaseous pressure, so the total *increase* in the vapour pressure is

$$\pi'' - \pi = \left(\frac{760 \times 22320\,\rho}{\lambda_0 M} - \pi\right)\frac{n}{N}.$$

In the second case of gases dissolved in liquids we have a substance like an aqueous solution of hydrochloric acid gas, which on distillation grows either richer or poorer in HCl till a certain strength of solution is reached. The solution then distils over unchanged. This is exactly analogous to the solution of one volatile liquid in another so we need not consider it separately.

38. Solutions of Liquids in Liquids. When we were considering solubility, we found that pairs of liquids must be divided into three classes—(i) those which will not mix at all, (ii) those partially soluble in each other, (iii) those soluble in each other in all proportions. The laws of vapour pressure are different for each case.

(i) With immiscible liquids the vapour pressure is equal to the sum of those of the constituents. This can be proved by passing the vapour of one boiling liquid into the other and examining the vapour which comes through, for in it the two substances will obviously be present in the ratio of their pressures. The sum of the two pressures will, at the boiling point of the mixture, be equal to the atmospheric pressure, so the boiling point must be lower than that of either constituent, but this is usually masked, for if one liquid forms a layer over the other, the mixture bumps violently if the more volatile liquid be below, while, if the positions are reversed, it is only the upper liquid which evaporates.

(ii) The behaviour of partially miscible liquids has been studied by Konowaloff[1], who found by experiment that the solution of a liquid A saturated with a liquid B exerts at a certain temperature the same vapour pressure as that which a solution of B saturated with A exerts at the same temperature. This can also at once be proved from theoretical considerations. For if we have an arrange-

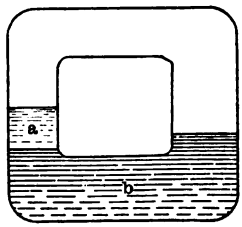


Fig. 7.

[1] *Wied. Ann.*, 1881, 14, p. 219.

ment like that in fig. 7 with a saturated solution of B in A at a, and a saturated solution of A in B at b, the vapour over each must have the same pressure and composition, or else distillation or diffusion would go on in the upper space; this would be compensated by diffusion through the liquids, and so a perpetual circulation would be kept up, which is impossible. Konowaloff measured the vapour pressures of mixtures of two liquids of varying composition and at different temperatures. The general result of his observations is shewn by the form of the

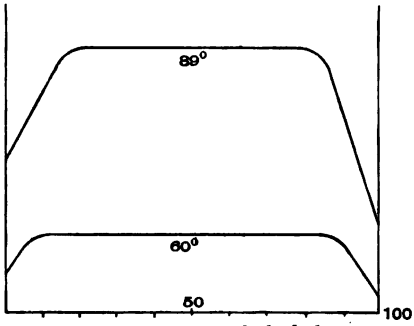


Fig. 8. Percentage of alcohol.

curve in fig. 8, which gives the relation between percentage composition (abscissæ) and vapour pressure (ordinates) of a mixture of water and isobutyl alcohol at 89° and 60°. While the percentage of alcohol is less than that required to saturate the water, the vapour pressure of the solution increases with the percentage of alcohol. When the solution is saturated, the vapour pressure is independent of the excess of alcohol present. Such a mixture has then a constant boiling point, and the composition of

the vapour is always the same. This constant vapour pressure is found to be smaller than the sum of those of the two constituents. When the percentage of alcohol is so large that all the water present can dissolve in it, the vapour pressure again alters with the composition of the solution, and finally sinks to its value for the pure alcohol. If a mixture represented by any point on either of the inclined portions of the curve be distilled, the composition of the vapour and the boiling point will gradually alter till the liquid present in large excess is finally left nearly pure. But as long as a heterogeneous mixture is present, the curve is a horizontal straight line, and the composition of the vapour and the boiling point remain constant.

(iii) The vapour pressures of mixtures of liquids which are soluble in each other in all proportions give curves which

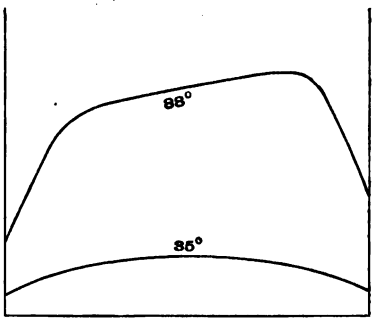


Fig. 9. Water and propyl alcohol.

gradually change from a form very like those given above to one quite different. The following curves are taken from Ostwald's *Lehrbuch*, and were drawn from Konowaloff's

numbers. They at once shew how the mixtures will behave on distillation. The tendency is (since there is no

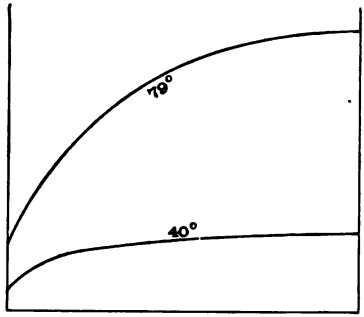


Fig. 10. Water and ethyl alcohol.

constancy in the composition of the vapour) for that particular mixture which has the greatest vapour pressure, and therefore the lowest boiling point, to come off first in greatest quantity, and therefore by repeatedly redistilling,

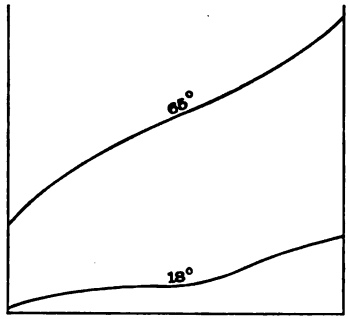


Fig. 11. Water and methyl alcohol.

we at last get a distillate which has the composition corresponding to this lowest boiling point. Thus with water and propyl alcohol, which mixture has a maximum

vapour pressure when the percentage of alcohol is about 75, the final distillate obtained will have that composition.

The curves for water with ethyl alcohol and with methyl alcohol shew that in these cases no maxima are reached, so that by repeated distillation we get a nearly pure alcohol in the receiver, and pure water is left in the retort after the first boiling. It is much easier to get

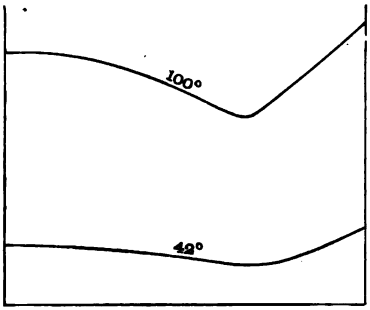


Fig. 12. Water and formic acid.

water free from alcohol than alcohol free from water, because the influence of a little alcohol on the boiling point of water is so much greater than that of a little water on the boiling point of alcohol. This case is of great importance in practice, for by such means mixed liquids of different boiling points are separated in the chemical laboratory by the process of "fractionation." We now see that this can only give perfect separation when the type of the vapour pressure curve is that shewn in figs. 10 and 11.

A mixture of water and formic acid shews the effect of considerable interaction between the constituents. The

vapour pressure of the mixture is lower than that of either constituent, and reaches a minimum at a percentage of alcohol of about 73. All other proportions will therefore tend to distil over sooner than this, and finally we shall get a residue left in the retort containing 73 per cent. of alcohol. This will then distil over unchanged.

The last case really includes such liquids as an aqueous solution of nitric or hydrochloric acid, which were once thought to shew definite chemical combination in the proportions of the mixture which finally distilled over unchanged. Roscoe[1] however proved that the composition of this distillate varied with change of pressure, and the facts are fully explained by the vapour pressure curves given above.

[1] *Quart. Journ. Chem.*, XII. p. 128, or *Treatise on Chemistry*, Vol. I. p. 188.

CHAPTER VII.

THE ELECTRICAL PROPERTIES OF SOLUTIONS.

39. Historical Sketch. As soon as the discovery of Volta's pile in the year 1800 became generally known, many investigations were made on its effects. The pile consists of a series of little discs of zinc, copper and blotting-paper moistened with water or brine, placed one on top of the other in the order zinc, copper, paper, zinc, &c., finishing with copper. Such an arrangement is really a primitive primary battery, each little pair of discs separated by moistened paper acting as a cell, and giving a certain difference of electric potential, the differences due to each little cell being added together and producing a considerable difference of potential or electromotive force between the zinc and copper terminals of the pile. Another arrangement was the crown of cups, consisting of a series of vessels filled with brine or dilute acid, each of which contained a plate of zinc and a plate of copper. The zinc of one cell was fastened by a screw to the copper of the next and so on, the isolated copper and zinc plates in the first and last cups forming the terminals of the battery.

Using a copy of Volta's original pile, Nicholson and Carlisle[1] found that when two brass wires leading from its terminals were immersed near each other in water, there was an evolution of hydrogen gas from one, while the other became oxidised. If platinum or gold wires were used, no oxidisation occurred, but oxygen was evolved as gas. They noticed that the volume of hydrogen was about double that of oxygen, and since this was the proportion in which these gases are contained in water, they explained the phenomenon as a decomposition of water. They also noticed that a similar kind of chemical action went on in the pile itself, or in the cups when that arrangement was used. Cruickshank[2] soon afterwards decomposed the chlorides of magnesia, soda and ammonia, and precipitated silver and copper from their solutions. He also found that the liquid round the pole connected with the positive terminal of the pile became alkaline and the liquid round the other pole acid. In 1806 Sir Humphry Davy[3] proved that the formation of the acid and alkali was due to impurities in the water. He had previously shewn that decomposition of water could be effected although the two poles were placed in separate vessels connected together by vegetable or animal substances, and established an intimate connection between the galvanic effects and the chemical changes going on in the pile. The identity of "galvanism" and electricity, which had been maintained by Volta, and had formed the

[1] *Nicholson's Journal*, 1800, 4, p. 179.
[2] *Ibid.*, 4, p. 187.
[3] Bakerian Lecture for 1806, *Phil. Trans.*

subject of many investigations, was finally established in 1801 by Wollaston, who shewed that the same effects were produced by both. In 1804 Hisinger and Berzelius[1] stated that neutral salt solutions could be decomposed by electricity, the acid appearing at one pole and the metal at the other, and drew the conclusion that nascent hydrogen was not, as had been supposed, the cause of the separation of metals from their solutions. Many of the metals then known were thus prepared, and in 1807 Davy decomposed potash and soda, which had previously been considered to be elements, by passing the current from a powerful battery through them when in a moistened condition, and so isolated the metals potassium and sodium.

The difference between the conduction of electricity through such bodies as these, and through metals and other solids, early engaged the attention of observers, and for some time the presence of water was thought to be necessary for electrolytic conduction. Faraday[2] however shewed that many bodies, including nearly all fusible salts which were non-conductors when solid, became electrolytes when fused, and just recently J. J. Thomson[3] and others have shewn that the passage of electricity through gases is an electrolytic action accompanied by chemical decomposition. The conditions necessary for electrolytic conduction in solutions will be discussed later.

The remarkable fact that the products of decomposition appear only at the poles, was perceived by the early

[1] *Ann. de Chimie*, 1804, 51, p. 167.
[2] *Experimental Researches*, Vol. I. 1833.
[3] *Recent Researches in Electricity and Magnetism*, 1893.

experimenters on the subject, who suggested various explanations. Grotthus[1] in 1806 supposed that it was due to successive decompositions and recompositions in the substance of the liquid. Thus if we have a compound AB in solution, the molecule next the positive pole is decomposed, the B atom being set free. The A atom attacks

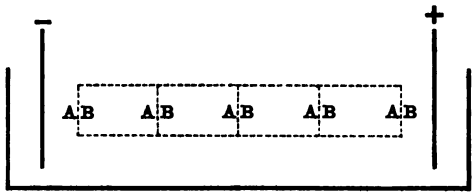


Fig. 13.

the next molecule, seizing the B atom and separating it from its partner which attacks the next molecule and so on. The last molecule in the chain gives up its B atom to the A atom separated from the last molecule but one, and liberates its A atom at the negative pole. Grotthus, and in fact nearly all the pioneers in the subject, thought that the decomposition was due to a direct attraction exerted by the poles on the opposite constituents of the decomposing compound, which varied as the square or some other power of the distance. This view was finally disproved by Faraday[2] who shewed that the electrical forces were the same at all positions between the poles, by placing two platinum strips, kept at a constant difference apart and connected through a galvanometer, at different positions in a trough of dilute acid through

[1] *Annales de Chimie*, 1806, 58, p. 54.
[2] *Experimental Researches*, 1833.

which a current was flowing. He also shewed that chemical decomposition could be produced without the presence of any metallic pole. An electric discharge from a sharp point connected with a frictional machine, was directed on to a strip of turmeric paper moistened with sulphate of soda solution, the other end of the paper being joined to the other terminal of the machine. Alkali appeared on the paper opposite to the discharging point. Another experiment shewed that insoluble hydrate of magnesia was produced at the junction between a strong solution of sulphate of magnesia and pure water when a current was passed across it. Faraday accepted the idea of Grotthus' chain, but held that there were chemical forces between atoms of opposite kinds in neighbouring molecules as well as in the same molecule, and that when the electric force was added to these they became strong enough to overcome the attractions between the atoms in the same molecule, so that a transfer of partners occurred. We shall see later that transfers of partners are probably always going on in solutions, whether a current is passing or not, and that the function of the electric forces is merely directive, but Faraday's account of the consequences of this interchange still holds good. He pointed out how it explained all the facts, including the passage of acids through alkalis under the influence of the current, a phenomenon which had created such surprise when discovered by Davy. Faraday shewed that the presence of the alkali not only facilitated the passage of the acid, but was even necessary, for, without something with which to combine on its way, the acid would be

unable to travel. Thus Faraday's view amounts to supposing a constant stream of acid in one direction and of alkali in the other.

Faraday introduced a new terminology which is still used. Instead of the word *pole* which implied the old idea of attraction and repulsion, he used the word *electrode*, and called the plate by which the current enters the liquid the *anode*, and that by which it leaves the *kathode*. The parts of the compound which travel in opposite directions through the solution he called *ions*—*kations* if they went towards the kathode and *anions* if they went towards the anode. He also introduced the words *electrolyte*, *electrolyse*, &c., which we have already used.

Faraday clearly pointed out that the difference between the effects of a frictional electric machine and of a voltaic battery lay in the fact that the machine produced a very great difference of potential, but could only supply a small quantity of electricity, while the battery gave a constant supply of an enormously larger quantity, but only produced a very small difference of potential.

40. Faraday's Laws. Davy had previously shewn that there was no accumulation of electricity in any part of a voltaic circuit, so that a uniform flow or current must be everywhere going on, and Faraday set himself to examine the relation between the strength of this current and the amount of chemical decomposition. He first proved by observations on the decomposition of acidulated water, that the amount of chemical action in each of

several cells was the same when the cells were joined together and a current passed through them all in series, even if the sizes of the platinum plates were different in each. The volume of *hydrogen* was unchanged even if electrodes of different materials—such as zinc or copper —were used. He then divided the current after it had passed through one cell into two parts, each of which passed through another cell before they were reunited. The sum of the volumes of the gases evolved in these two cells was equal to the volume evolved in the first cell. The strength of the acid solution was then varied, so that it was different in the different cells in one series, but the chemical action still remained the same in all. Thus the deduction was made that *the amount of decomposition was proportional to the quantity of electricity which had passed.* An apparatus for the decomposition of water can therefore be used to measure the total quantity of electricity which has passed round a circuit. Such instruments are termed *voltameters.*

The same law was then shewn to be true for solutions of various metallic salts, and also for salts in a state of fusion—the weight of metal deposited being always the same for the same quantity of electricity. A second law also was discovered, namely that *the mass of an ion liberated by a definite quantity of electricity is proportional to its chemical equivalent weight.* In the case of elementary ions this *equivalent* weight is the *atomic* weight divided by the valency, and in the case of compound ions it is the *molecular* weight divided by the valency.

It was then proved that the mass of zinc consumed

in each cell of the battery was the same as that deposited by the same current in an electrolytic cell placed in the external circuit.

These results may be grouped in one statement which is known as Faraday's law of electrolysis.

The mass of an ion liberated by a current is proportional to the whole quantity of electricity which passes and to the electro-chemical equivalent of the ion, the electro-chemical equivalent being proportional to the chemical equivalent weight.

By later investigations it has been found that the mass of hydrogen liberated by one electro-magnetic unit of electricity is $1{\cdot}0352 \times 10^{-4}$ gram. The electro-chemical equivalent of any other ion can be found by multiplying this figure by its chemical equivalent weight. By measuring the quantity of electricity which passes in electro-magnetic units and calling it q, we can therefore write an expression for the mass liberated

$$m = 1{\cdot}0352 \times 10^{-4} \epsilon q,$$

where ϵ is the chemical equivalent weight.

Faraday's law has been confirmed in the case of silver to a great degree of accuracy by Lord Rayleigh and Mrs Sidgwick[1], who gave the value 0·0111795 for its electro-chemical equivalent, and in the case of copper by W. N. Shaw[2]. In the latter case small variations occurred on altering the intensity of the current, but they were traced to the action of the copper sulphate solution in

[1] *Phil. Trans.*, 1884, (2), p. 411.

[2] *British Association Report*, 1886, p. 318.

dissolving the newly precipitated copper. Faraday himself considered that in certain cases a small current could leak through electrolytes without chemical decomposition[1], but it is very doubtful whether such can be the case.

One or two consequences of these laws must now be traced. Since many elements (iron for example) have different equivalents in their different series of compounds, their electro-chemical equivalents must also vary. Thus if a current be sent through two cells in series, one containing the solution of a ferrous and the other the solution of a ferric salt, the quantity of iron liberated in the first cell will be proportional to 56/2 or 28, and the quantity liberated in the second will be proportional to 56/3 or 18·7, since the atomic weight of iron is 56.

Since unit quantity of electricity in passing through an electrolyte always decomposes a mass of the substance equal to $1{\cdot}0352 \times 10^{-4}\epsilon$, it follows that a definite quantity of electricity is always associated with the same number of equivalents. We can in fact represent electrolytic conduction as a process of convection, a positive charge being carried by the kations in one direction, and a negative charge by the anions in the other, and it follows that the charge on a univalent ion is always the same whatever be the nature of the ion, and the charge on a divalent ion is twice, and that on a trivalent ion three times that carried by a univalent ion. From the equation on p. 110 we see that the charge carried by the number of the two opposite univalent ions contained in one

[1] *Exp. Researches*, 1834, series 8, §§ 970, 984.

gram-equivalent of a simple binary compound like NaCl, is (since $m = \epsilon$)

$$q = \frac{1}{1{\cdot}0352 \times 10^{-4}} = \frac{1}{\eta},$$

where η is the electro-chemical equivalent of the standard substance hydrogen.

41. Polarisation. It was soon observed that a single cell of Volta's crown of cups was not able to decompose water, and that a certain considerable difference of potential had to be kept up in order to drive a permanent current through an electrolytic apparatus. This subject was investigated by Faraday, who referred the effect to the chemical affinity between the parts of the water, which needed a force greater than that affinity in order to separate them. If we use a sufficient electromotive force, and send a current between platinum plates in acidulated water, the plates will be found to be in a peculiar condition (which is known as *polarisation*) and to have acquired the power of driving a current for some time in the reverse direction, if they are disconnected from the primary battery and joined to each other through a galvanometer. If the electromotive force between the polarised plates be determined, it will be found to be 1·47 volts, and this may be taken to measure the affinity of hydrogen and oxygen, so that no primary battery or other source of electrical energy is able to send a permanent current through acidulated water unless the electromotive force that it gives is at least 1·47 volts, and it is important to observe that the effective electromotive

force acting round such a circuit is that of the battery *less* 1·47 volts. This reverse electromotive force must always be taken into account in calculating the strength of a current, when there is any polarisation in the circuit. If the applied electromotive force is less than the critical value, some current will at first pass, but this gradually becomes less, and finally nearly vanishes as the electrodes become polarised. A *very* small current always appears to leak through, but whether this is due, as Faraday supposed, to some conduction without decomposition is extremely doubtful. It must be remembered that both oxygen and hydrogen are to some extent soluble in water, so that some of the gases set free are dissolved, and may so escape into the air and make room for more. In other cases, in which bodies like chlorine are evolved, the products of electrolysis may meet by diffusion of one or both through the solution and recombine; a little more decomposition would then go on to supply their place, and so a permanent, though very small, leakage current would be kept up. The accurate measurement of the reverse electromotive force of polarisation presents some difficulty. It rapidly falls off in intensity and the reversal of the connections must be quickly made in order to get its maximum value. Raoult[1] found that a speed of reversal equal to 100 per second was enough to secure this.

42. Accumulators. Polarisation is the principle which underlies the action of all secondary cells or accumulators. If an ordinary water voltameter, with the platinum

[1] *Ann. de Chimie et de Phys.*, 1864, [4], 2, 326.

electrodes resting partly in the solution and partly in the evolved gases, be connected with a galvanometer, we shall find that a reverse current is set up, and will continue to flow as long as any of the evolved gases (which will gradually disappear) remain. This is Grove's gas battery. If two lead plates be immersed in dilute sulphuric acid and a current passed between them, the anode becomes coated with brown dioxide of lead, and spongy metallic lead is deposited on the kathode. The reverse electromotive force of this arrangement is about 2·0 volts. For practical purposes the cells are much improved if currents be passed through them for some time as a preliminary, first in one direction and then in the other. This treatment increases the effective area of the lead plates, and so enables them to store a larger amount of chemical energy. These lead cells, originally due to Planté (1860), are universally employed in one of their many forms. The modifications which have been introduced have mainly been directed to increasing the effective area of the plates by making them in the form of a lattice-work or by coating them with red lead.

43. Primary Cells. Just as polarisation is set up in an electrolytic apparatus placed in the external circuit, so it is produced in the cells of the battery itself, when these consist of a plate of zinc and a plate of platinum or copper placed in acidulated water. Bubbles of hydrogen appear at the platinum plate, and the reverse electromotive force which they set up soon causes the current to decrease in strength. Many forms of cell have been de-

vised to obviate this. In some, oxidising agents such as bichromate of potash are added to the liquid, while in others the platinum plate is put inside a porous pot, and surrounded by oxidising agents (such as nitric acid in Grove's cell), or by a solution of copper sulphate which causes copper to be deposited on the electrode: in this case itself of copper (Daniell's cell). By some such device a fairly constant electromotive force can be obtained. It is worthy of note that if a current be forced through a Daniell's cell *against* the electromotive force of the cell, copper will redissolve to form copper sulphate, while zinc will be deposited on the zinc electrode from the zinc sulphate solution. The processes which go on in Daniell's cell are therefore perfectly *reversible*.

It is interesting to examine the conditions necessary for the solution of zinc. Pure zinc, or ordinary zinc which has been amalgamated with mercury, will not dissolve in dilute sulphuric acid, but if a piece of another less oxidisable metal like platinum be put into the liquid in contact with the zinc, solution at once begins, zinc sulphate is formed and hydrogen is evolved at the surface of the platinum. A complete voltaic circuit is thus necessary, and a quantity of electricity equivalent to the amount of chemical action, flows round it. If a piece of pure zinc be placed in a neutral solution of zinc sulphate, no action occurs even in presence of platinum, but solution at once begins if a few drops of acid be added. Ostwald[1] observed that if the zinc and platinum were separated by a porous partition, and connected by a wire outside the solution of

[1] *Phil. Mag.*, 1891, 32, p. 145.

zinc sulphate, no action occurred if acid was added to the vessel containing the zinc, but that the zinc was at once attacked if the acid was put into the vessel containing the platinum. In the first case, supposing the zinc replaces the hydrogen in the acid, the hydrogen must again form sulphuric acid in contact with the zinc sulphate round the platinum plate, and zinc must be there deposited. There is thus no resultant chemical action, and no supply of energy to keep up the current. In the second case, however, hydrogen is evolved at the platinum, being replaced in the sulphuric acid by zinc from the zinc sulphate. This action gives a supply of energy, and can therefore go on spontaneously.

44. Contact Difference of Potential. The source of the energy of a voltaic cell is unquestionably the chemical action which goes on, but much discussion has taken place about the exact seat of the difference in potential. Volta thought that it was produced at the contact between the pair of metals, and arranged his pile in the order zinc, copper, paper, zinc... on this supposition. If a piece of zinc connected with one pole of an electrometer be put in contact with a piece of copper connected with the other, a difference of potential is certainly observed, and this may amount to about 0·8 volt. It must be remembered, however, that the apparatus is in contact with air, which may exert an oxidising action, and experiments conducted in absence of air, or in artificial atmospheres of other gases, have led to no definite results, probably owing to the difficulty of getting rid of the last traces of air. An indirect method of measurement, used

by Jahn[1], avoids this difficulty. Peltier found that when a current of electricity was passed across the junction between two metals, a reversible evolution or absorption of heat occurred. By the principles of thermodynamics it follows that an electromotive force must reside there, and by measuring the strength of the current and the total thermal evolution its value can be calculated. Jahn's results shewed that it was always small, and rarely amounted to more than a few thousandths of a volt. This appears to disprove the existence of any difference of potential of the order of 0·8 volt, and, though some doubt has been thrown on the validity of the reasoning, it is improbable that the great electromotive force observed by the other method could be so nearly balanced as to disappear in the Peltier effect.

Faraday's work led many people to believe that the true seat of the difference in potential, like the source of the energy of the current, was to be found at the junction between metal and liquid, and this appears to be the more probable view. This again is a difficult thing to observe, for, in order to get the potential of the liquid by any of the ordinary methods, we must introduce a wire leading to an electrometer, which gives a new surface of contact, and therefore another difference of potential. The only way in which this difficulty has been surmounted is due to Lippmann[2]. It is found that when the surface of separation between mercury and dilute sulphuric acid is increased, a current is produced, and conversely if an

[1] *Wiedemann's Annalen*, 1888, 34, p. 755.

[2] *Pogg. Ann.*, 1873, 149, p. 561; *Ann. de Chim.*, 1875, [5], 5, p. 494.

external electromotive force be applied by passing a current across it, that the area of the surface tends to alter, owing to a change in the effective surface tension caused by the polarisation at the junction. These phenomena have been utilised by Lippmann in the construction of electrometers. Several forms are used[1]—in one a vertical glass tube is drawn off to a very fine capillary the end of which is bent upwards. This apparatus is filled with mercury, and the lower part immersed in a vessel of dilute sulphuric acid whose bottom is covered with a layer of mercury. The capillary forces tend to depress the mercury surface in the little tube, and are balanced by the pressure of the long column. When the mercury in the vertical tube, and the mercury in the bottom of the vessel of acid, are kept at different potentials, the surface tension at the junction between mercury and acid in the capillary tube changes, and the level of the junction is altered. A microscope is arranged to observe this, and for small differences, the change in the level is found to be proportional to the difference of potential.

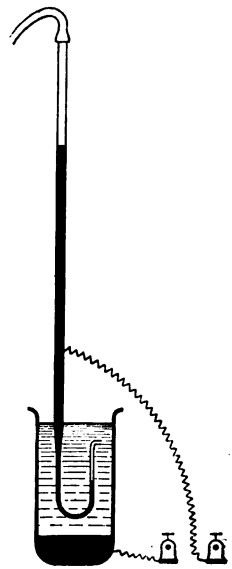


Fig. 14.

These phenomena have been explained by von Helmholtz[2]. The difference of potential between a metal and

[1] See Ostwald's *Physico-Chemical Measurements*.

[2] *Wied. Ann.*, 1882, 16, p. 35.

an electrolyte must cause an electrification over the boundary between them, positive electricity accumulating on the mercury surface, and negative electricity on the acid. Each side of this "double layer of electricity" will try to increase its area owing to the repulsion between the different portions of the similar charge, so that the effect of the double layer will be opposite to that of the surface tension, which tends to diminish the area. If then we have mercury in contact with dilute sulphuric acid, and increase the difference of potential between them by external means, the surface tension will be still further reduced. If, however, we reverse our external electromotive force, so that we make the mercury less and the acid more positive, the effect of the natural double layer will be reduced, and the surface tension will increase. This will go on until the external potential difference is equal and opposite to that of the natural double layer, when the surface tension will be a maximum. Beyond this another double layer will be formed of opposite sign—the mercury becoming negative and the acid positive—and a reduction in surface tension will again take place. Thus by measuring the external difference of potential required to give the surface tension its maximum value, the difference of potential due to the natural double layer formed on contact was found by Lippmann to be about 0·9 volt.

This has been confirmed in two ways. If the surface of contact be increased by mechanical means, the double layer will be stretched, the potential difference will be reduced and a current will flow in order to again increase

it to its normal value. But if the potential difference be destroyed by an external electromotive force, this will cease to hold, and no current will be observed on increasing the surface. Pellat[1] found that the current ceased to be produced when an external electromotive force of about 1·0 volt was applied.

When mercury is dropped from a fine orifice in a glass vessel the lower part of which is placed in an electrolyte, it must in the end assume very nearly the potential of the liquid; for as each drop falls, it will form a double layer round it, and in order to do this, it must take positive electricity from the stock of mercury, and so reduce its potential nearly to that of the liquid. It will never quite reach that value, because it is all the time trying to set up the usual difference of potential by contact, but by making the formation of the drops rapid, the discharge of electricity from the stock of mercury can be made nearly perfect. In this way Ostwald[2] obtained a difference of potential between the drops and the mercury at rest of about 0·81 volt.

The maximum value of the surface tension, produced by applying an external electromotive force sufficient to destroy the double layer, is the real surface tension free from all electrical disturbances, and this was found by Ostwald to be independent of the nature of the electrolyte, while the natural value as usually measured varies greatly.

When we know the true difference of potential

[1] *Comp. Rend.*, 1887, 104, p. 1099.

[2] *Zeits. f. physikal. Chemie*, 1887, 1, p. 583.

between mercury and any given electrolyte, we can find the value for a surface between that electrolyte and any other metal, by measuring the electromotive force of the combination mercury-electrolyte-metal. Assuming that the effect at the junction of the metals is small, this gives the sum of the effects at the junctions mercury-electrolyte and electrolyte-metal, and from this the latter can be found by subtraction. The following table gives the potentials of different metals in normal solutions, the potential of the electrolyte being put equal to zero.

	HCl	HBr	HI	H_2SO_4
Zn	− 0·54	− 0·46	− 0·30	− 0·62
Cd	− 0·24	− 0·18	− 0·08	− 0·22
Sn	+ 0·02	+ 0·12	+ 0·28	− 0·02
Pb	+ 0·03	+ 0·10	+ 0·26	− 0·04
Cu	+ 0·35	+ 0·35	+ 0·36	+ 0·46
Bi	+ 0·41	+ 0·47	+ 0·60	+ 0·46
Sb	+ 0·51	+ 0·60	+ 0·54	+ 0·48
Ag	+ 0·57	+ 0·51	+ 0·45	+ 0·73
Hg	+ 0·57	+ 0·50	+ 0·44	+ 0·86

Thus the initial electromotive force of a zinc-copper couple, 1·08 volt, is produced by a difference of potential of 0·62 between the zinc and acid and of 0·46 between the acid and copper.

The cause of these differences of potential has been explained by W. Nernst on the supposition that each metal in contact with a given electrolyte possesses a certain "solution pressure," analogous to the vapour pressure of

a liquid, by reason of which ions are detached from it, and go into solution carrying their charges with them and leaving the metal oppositely electrified. The development of this idea will be described when we are considering the Dissociation Theory in Chapter XI.

It is worthy of note that cells with different positive terminals (copper, platinum, &c.) give different electromotive forces, although the chemical actions are the same, consisting in each case of the solution of zinc and the evolution of hydrogen. The differences arise from the fact that, in order to set free the hydrogen, different electromotive forces have to be overcome at the electrode, so that different fractions of the whole energy are used to keep up the electromotive force.

45. Source of the Energy of the Current, and Theory of the Voltaic Cell. As we have already remarked, the supply of energy necessary to drive the current is drawn from the chemical energy liberated by the actions which go on in the cell.

When a quantity of electricity q passes round the circuit, the total amount of energy liberated by the chemical action which goes on can be calculated from the heats of formation of the various chemical compounds produced, which have in most cases been experimentally determined by Thomsen and others. If H be the heat (measured in mechanical units) which would be liberated if all the energy produced when one unit of electricity passes, assumed the thermal form, then the total energy is qH, and if all this energy were used in forcing the current

round the circuit, we should have the equation which Lord Kelvin[1] deduced from Joule's principle

$$qH = qE \quad \text{or} \quad H = E,$$

where E is the electromotive force. In nearly all cases however the electromotive force of a cell changes with temperature, and if this is the case it is easy to shew from the principles of thermodynamics that a reversible heat evolution or absorption will occur on the passage of a current. In order to prevent this from producing changes in temperature, heat must be supplied or abstracted, and one side of our equation must be increased or diminished by the mechanical equivalent of this heat.

The relation is at once deducible if we imagine a cell, in which the chemical processes are all reversible, put through a thermodynamical cycle of changes. Let us begin by supposing that we place our cell in an enclosure whose temperature is T and that we let pass a quantity of electricity q through the cell in the direction of the electromotive force. The cell will do a quantity of work Eq. Suppose that in order to keep its temperature constant we supply hq units of heat. Then let us put the cell into a second enclosure which is at a temperature $T - \delta T$, very slightly lower than the first. If the electromotive force is unchanged, the work done *on* the cell in forcing q units of electricity through it against the electric forces, will be Eq, so that the whole gain of work throughout the cycle is nil, and no heat is required to keep the temperature constant. If, however, E changes with the temperature

[1] *Philosophical Magazine*, 1851, [4], 2, p. 429.

so that dE/dT represents its *rate of change*, we shall have for the electromotive force of the cell at a temperature $T - \delta T$

$$E' = E - \frac{dE}{dT}\delta T,$$

so that the work done will now be

$$\left(E - \frac{dE}{dT}\delta T\right) q.$$

We now have the cell in exactly the same state as at first, for forcing the q units backwards through it has reversed all the chemical changes. We can therefore apply the principles of thermodynamics, and are able to use the ordinary relation that the effective gain of work during the cycle is to the amount of heat absorbed in the hot enclosure as the difference in temperature is to the absolute temperature. Now the gain of work is evidently

$$Eq - \left(E - \frac{dE}{dT}\delta T\right) q = \frac{dE}{dT}\delta T \,.\, q,$$

and so we get

$$\frac{\frac{dE}{dT}\delta T \,.\, q}{hq} = \frac{\delta T}{T},$$

$$\therefore h = T\frac{dE}{dT},$$

which gives the mechanical equivalent of the heat necessary to keep the temperature constant when one unit passes. Since T is always a positive quantity, it follows that the sign of h is the same as that of dE/dT, and so, if the electromotive force increases as the

temperature rises, the sign of h is positive and heat must be supplied to the cell. If the electromotive force decreases as the temperature rises, heat must be taken from the cell.

Thus the chemical energy of the materials has other work to do than was at first supposed, and we must put

$$H = E + h = E + T\frac{dE}{dT},$$

or

$$E = H - T\frac{dE}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (24),$$

an equation for the electromotive force of a cell first given by von Helmholtz[1], and experimentally confirmed by Czapski[2] and Jahn[3].

Let us calculate by this method the electromotive force of a Daniell's cell. When unit quantity of electricity passes, the chemical changes are these:—$32{\cdot}5 \times 1{\cdot}0352 \times 10^{-4}$ grams (the electro-chemical equivalent) of zinc dissolve in dilute acid, the hydrogen evolved from this ($1{\cdot}0352 \times 10^{-4}$ gram) displaces $31{\cdot}6 \times 1{\cdot}0352 \times 10^{-4}$ grams of copper from copper sulphate, and this same amount of copper is liberated. The heats of formation are given in any book on chemistry—we shall take them from Ostwald's *Lehrbuch*. When zinc sulphate is formed from its elements, the amount represented in grams by the formula $ZnSO_4$ evolves 230000 calories of heat, and its solution in water 18500 cals. In the same way the heat

[1] *Berl. Ber.*, 1882, pp. 22, 825, and *Wissenschaftliche Abhandlungen*, 2, p. 962.

[2] *Wied. Ann.*, 1884, 21, p. 209.

[3] *Wied. Ann.*, 1886, 28, pp. 21, 491 and 1888, 34, p. 755.

of formation of sulphuric acid, H_2SO_4, is 193100 cals. and its heat of solution 17800 cals. The net result of the action $Zn + H_2SO_4 = ZnSO_4 + H_2$ is therefore the evolution of 37600 cals. of heat. Finally we have the action $H_2 + CuSO_4 = H_2SO_4 + Cu$. Now the heat of formation of $CuSO_4$ is 182600 cals. and its heat of solution 15800. The net result of the change is got by subtracting from the sum of these the sum of the corresponding numbers for sulphuric acid: it comes out -12500 cals. Since the $CuSO_4$ is not *formed* but *decomposed*, we must subtract this from the 37600 cals. to get the total change throughout the cell, which equals 50100 cals. This is the heat change corresponding to the solution of 65 grams of zinc, so that when one electro-chemical equivalent is dissolved the thermal evolution is

$$\frac{50100 \times 32{\cdot}5 \times 1{\cdot}0352 \times 10^{-4}}{65} = 2{\cdot}592 \text{ cals.}$$

The temperature coefficient of a Daniell's cell is very small, so that dE/dT can be neglected, and equation (24) becomes

$$\begin{aligned} E &= 2{\cdot}592\, J \\ &= 2{\cdot}592 \times 4{\cdot}2 \times 10^7 \\ &= 1{\cdot}09 \times 10^8 \text{ electro-magnetic units} \\ &= 1{\cdot}09 \text{ volts,} \end{aligned}$$

a number agreeing extremely well with observation.

CHAPTER VIII.

ELECTRICAL PROPERTIES (*continued*).

46. The Nature of the Ions. The work of Berzelius, beginning in 1804, on the electrolytic decomposition of neutral salts, led him to frame a theory which regarded all chemical action as brought about by the electric forces between oppositely charged atoms. When two atoms united, he supposed that the charges were not exactly neutralised, and the group of atoms was left with a balance of positive or negative electricity, and so could still combine with other atoms or groups of atoms. He regarded each chemical compound as formed by the union of an electro-positive group with an electro-negative group, and held that the action of the electric current in producing acid round the anode, and alkali round the kathode of a neutral salt solution, was to be explained simply as a direct separation of the salt into acid and base. When the attention of chemists began to be directed more to organic chemistry, the dualistic ideas of Berzelius had to be abandoned, and even from the physical side objections were soon raised. Thus

Daniell[1] shewed that in the electrolysis of a solution of sodium sulphate an equivalent of hydrogen was produced as well as an equivalent of acid and base. This is at once reconciled with Faraday's law if we suppose that the parts of the salt, from an electrolytic point of view, are Na and SO_4, and that the hydrogen results from a secondary action of the sodium on the water of the solution.

In some cases, the phenomena of electrolysis give valuable information about the nature of the body in solution. We are able, for instance, to distinguish between double salts and salts of compound acids. Thus Hittorf shewed that when a current was passed through a solution of potassium platinichloride, the platinum appeared at the anode. The salt must therefore be derived from a compound acid, and have the formula Na_2PtCl_6, the ions being sodium and $PtCl_6$, for if it were a double salt it would decompose as a mixture of sodium chloride and platinum chloride, and both metals would go to the kathode.

47. Secondary Actions. Owing to these secondary actions it is often difficult to determine what are the real ions in any given case of electrolysis, for the parts into which the electrolyte is primarily resolved, and which travel through the solution, when they reach the electrode and are set free, may attack the substance of the electrode, or some constituent of the solution, and form secondary products. Thus the final products of the decomposition are often quite different from the ions,

[1] *Phil. Trans.* 1839, 1, p. 97 and 1840, 1, p. 209.

and chemical analysis of the solution round the electrodes then gives only indirect evidence as to their nature. In the case of a solution of potash, for example, the ions are K and OH. When the kation K reaches the electrode, instead of being set free in the metallic state, it attacks the water, liberating hydrogen and again forming potash, and the anion OH produces water and oxygen at the anode. Thus the final products are the same as though water had been directly decomposed.

This leads us to examine more closely the part played by water in electrolysis. It was at first thought to be the only active body, and to be necessary in every case of electrolytic decomposition. The dilute acid or alkali which was always added when water was to be decomposed, was supposed merely to allow the passage of the current by reason of its conductivity, and it was imagined that the current then directly decomposed the water. Now pure water is known to be a very bad conductor, though when great care is taken to remove all dissolved bodies, there is evidence to shew that some part of the small trace of conductivity remaining is really due to the water itself. Thus F. Kohlrausch[1] has prepared water whose conductivity in C.G.S. units was $1{\cdot}8 \times 10^{-11}$ at 18° C. Even here some little impurity was present, and Kohlrausch estimates that the conductivity of chemically pure water would be $0{\cdot}36 \times 10^{-11}$ at 18° C. As we shall see later, the conductivity of very dilute salt solutions is proportional to the concentration, so that it is probable that in most

[1] See § 78.

cases practically all the current-carrying is done by the salt. It seems probable then that what is called the decomposition of water is really a secondary effect due to the presence of the acid. Thus, if sulphuric acid is used, the primary ions are probably hydrogen and sulphion, SO_4. This latter, instead of being set free, decomposes the water, again forming sulphuric acid and liberating oxygen. This reasoning is confirmed by the fact that if the acid is strong, sulphur dioxide is evolved—if the water were the active agent it would still furnish the final product, even when present in very small quantities. The same kind of thing occurs with hydrochloric acid dissolved in water. While the solution is strong, hydrogen and chlorine are evolved, but as it becomes dilute the chlorine is gradually all taken up by the water, oxygen being liberated. The part played by the water will be again considered in Chapter XI.

The electrolysis of mixed solutions is probably another case of secondary action. When two salts are dissolved together in water, and a current passed through the liquid, it is generally found that, unless the current is very strong, the less oxidisable metal is alone deposited at the kathode. But if we imagine the ions to convey the current by a process of convection, we must suppose that the ions of both salts are travelling through the liquid, since the electric forces act on both alike. This was experimentally confirmed by Hittorf[1] by measurements of the conductivity of a mixed solution. When the more oxidisable metal reaches the kathode, however,

[1] *Poggendorf's Annalen*, 1858, ciii. p. 48.

it acts on the solution and replaces the less oxidisable metal, just as a strip of zinc placed in copper sulphate solution precipitates the copper. When the current is increased, and the chemical action is rapid, there is no time for this process to take place, and both metals appear on the electrode. The readiness with which an ion acts on the solution, when it is liberated at the electrode by the electric forces, has been taken advantage of by Becquerel and others in order to prepare many new and interesting chemical compounds.

48. Practical Applications of Electrolysis. In this book any detailed account of the practical applications of electrolysis would be entirely out of place, but it is interesting to remark that just as the strength of current used may influence the secondary actions which go on, so it may also influence the physical state in which a metal is deposited. This explains why in the processes of electroplating, &c. it is necessary to carefully adjust the current density (that is the strength of the current per unit area of the electrode) in order to prevent the deposit from being crystalline, or from being deposited so fast that it only loosely adheres to the plate.

The fact that the less oxidisable metal is usually first deposited from solution has often been used to effect the separation of metals, and the process has lately been developed on the large scale for the deposition of pure copper from an impure solution of its salts.

49. Complex Ions. In a normal case of electrolysis, such as that of an aqueous solution of potassium

chloride, it is probable that the primary ions are the simple bodies K and Cl, but in a few cases, such as that of cadmium iodide dissolved in alcohol, very great changes of strength occur in the solution near the electrodes (see p. 135), and it seems necessary to suppose that some unaltered salt is attached to the anion. The ions will then be Cd and $I_2(CdI_2)$, the latter being complex. It has even been suggested that molecules of the solvent may also be attached to ions, and be dragged along by them under the influence of the electric forces[1].

50. The Migration of the Ions. Having obtained some idea of the nature of the ions, we must now enquire whether it is possible to obtain any information about the velocity with which they travel through the solution.

If we pass a current from copper plates through a solution of copper sulphate, we shall notice that the colour of the liquid in the neighbourhood of the anode becomes deeper, and in the neighbourhood of the kathode lighter in shade. This is well seen if the electrodes are arranged horizontally with the anode underneath. When the electrodes are of copper, the quantity of metal in solution remains constant, since it is dissolved from the anode as fast as it is deposited at the kathode, but if we use platinum electrodes, the quantity in solution becomes continually less, and in this case more salt is taken from the neighbourhood of the kathode than from near the anode, and the colour of the solution, therefore, becomes pale more rapidly near the kathode than near the anode.

[1] See W. N. Shaw on Electrolysis, *B. A. Report* 1890, p. 201.

Two explanations of this seem possible. The first is to suppose that (as in the case of cadmium iodide in alcohol) the ions are really complex, unaltered salt being attached to the anion or solvent to the kation, so that salt is drawn to the anode or solvent to the kathode. The second explanation (due to Hittorf[1]), is that the velocity of the ions is different—the anion, in the case of copper sulphate, travelling faster than the kation.

Let us develope the consequences of Hittorf's hypo-

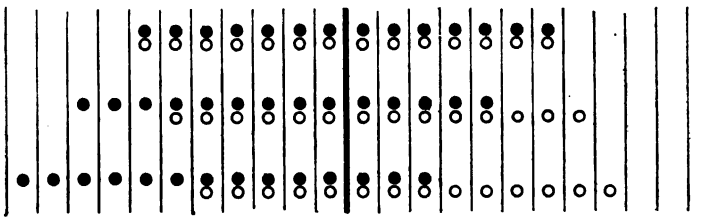


Fig. 15.

thesis by the method given by Ostwald. In fig. 15 the black dots represent the one ion, and the white circles the other. Let the black ions move to the left twice as fast as the white ions move to the right. While the black ions move over two of our spaces, the white ones move over one. Two of these steps are represented in the diagram. At the end of the process it will be found that six molecules have been decomposed, six black ions being liberated at the left and six white ions at the right. Looking at the combined molecules, however, we see that while five remain on the left side of the middle line, only three are still present on the right. Thus the left-hand

[1] *Pogg. Ann.*, 1853—9, 89, p. 177, 98, p. 1, 103, p. 1, 106, pp. 337, 513.

side, towards which the faster ions moved, has lost two combined molecules, while the right-hand side, towards which the slower ions travelled, has lost four—just twice as many. Thus we see that the ratio of the masses of salt lost by the two sides is the same as the ratio of the velocities of the ions leaving them. Therefore, by analysing the contents of a solution after a current has passed, we can calculate the ratio of the velocities of its two ions. A long series of measurements of this kind has been made by Hittorf[1], Loeb and Nernst[2] and others, who used various forms of apparatus arranged so as to enable the anode and kathode solutions to be separately examined after the passage of the current. Hittorf called the phenomenon the "migration of the ions," and expressed his results in terms of a migration constant which gives the amount of salt taken from the neighbourhood of one electrode as a fraction of the whole amount decomposed. It also expresses the ratio of the velocity of one ion to the sum of the opposite ionic velocities. All known results on the subject have been collected by T. C. Fitzpatrick in his tables of "The Electro-Chemical Properties of Aqueous Solutions," published in the British Association Report for 1893, and reprinted by permission in the appendix to this book. From these tables the following numbers are selected. They represent the migration constant for the anions. Thus $CuSO_4$ ·638 means that the velocity of the SO_4 ion is to the sum of the two velocities as ·638 : 1, and is therefore to the velocity of the Cu ion as ·638 : ·362.

[1] *Pogg. Ann.*, 1853—9. Vol. 89, p. 177, 98, p. 1, 103, p. 1, 106, pp. 337, 513.

[2] *Zeits. f. physikal. Chemie*, 1888, 2, p. 948.

Migration Constants.

Substance	Concentration of solution in gram equivalents per litre	Migration constant for anion
Hydrochloric Acid	·0128	·210
	·33	·161
	2·64	·193
	7·34	·319
Potassium Chloride	·03	·503
	2·55	·516
Sodium Chloride	·162	·628
Sodium Nitrate	·125	·615
	3·5	·600
Sulphuric Acid	·126	·206
$\frac{1}{2}H_2SO_4$	3·48	·174
	10·8	·288
Sodium Sulphate	·276	·634
	1·18	·641
Copper Sulphate	·0846	·638
	·692	·675
	1·962	·724
Cadmium Iodide in Alcohol	1 part in 1·107	2·102
	„ „ 37·23	1·318

The migration constant for cadmium iodide dissolved in alcohol shews that some unaltered salt must be conveyed through the solution, and has led to the supposition of the existence of complex ions.

51. The Velocities of the Ions. Thus from Hittorf's migration constants we can find the ratio of the velocities of the two ions in any given case, but in order to find the absolute value of these velocities we must get some other relation between them. F. Kohlrausch pointed out[1] that such a relation could be deduced from a knowledge of the conductivity of the solution.

[1] *Wied. Ann.*, 1879, 6, pp. 1, 145, 1885, 26, p. 161 and 1893, 50, p. 385.

Let u and v be the ionic velocities of the kation and anion respectively, so that $u+v$ is their relative velocity, that is the velocity with which they are dragged past each other by a certain electric force. This force will be measured by the rate at which the electric potential falls off per unit of length as we go from one electrode to the other—by what we may call the potential gradient, dV/dx.

If there are N gram-equivalents of electrolyte in one cubic centimetre, when the ions travel past each other with a speed $u+v$, they cause a total quantity of electricity of $N(u+v)/\eta$ (see p. 112) to flow in one second across unit area normal to the direction of motion. But this is equal to the current per unit area, and since Ohm's law holds good for electrolytes (see p. 143) we can also put the current equal to $k.dV/dx$ where k denotes the conductivity, i.e. the reciprocal of the specific resistance.

$$\therefore (u+v)\frac{N}{\eta} = k\frac{dV}{dx},$$

or

$$u+v = \frac{\eta k}{N}\cdot\frac{dV}{dx} \quad \text{.....(25).}$$

η, the electrochemical equivalent of hydrogen, is $1{\cdot}0352 \times 10^{-4}$; for a potential gradient of one volt per centimetre (which is the unit most often used) we must put

$$\frac{dV}{dx} = 10^8 \text{ C.G.S. units,}$$

so that for this gradient $u+v = 1{\cdot}0352 \times 10^4 \frac{k}{N}$.

If n is the number of gram-equivalents per *litre*, $n = 1000N$ and

$$u+v = 1{\cdot}0352 \times 10^7 \frac{k}{n} \text{ ..... (26).}$$

In order to find k/n, which he called the molecular

conductivity, Kohlrausch made a long series of determinations of the specific electrical resistances of salt solutions. These will be fully described later (p. 145). At present we need only notice that, as the dilution increased, the values of k/n rose, approached a limiting value, and finally at very great dilution became constant. For very weak solutions, then, the value of $u+v$ is a constant. Now if we know $u+v$, and also the ratio u/v, we can get absolute values for both velocities, and at great dilution these will be constants, independent of the concentration. Kohlrausch found, if he calculated the values of this limiting velocity for any one ion from observations on the solutions of two or more substances containing it, that they came out the same. Thus the velocity of the chlorine ion was, at great dilutions, the same in solutions of the chlorides of potassium, sodium and lithium. This is shewn by the following table.

Ionic Velocities in 10^{-6} *cms. per sec. at* 18° C. *calculated for a potential gradient of* 1 *volt per cm.*[1]

	KCl			NaCl			LiCl		
n	$u+v$	u	v	$u+v$	u	v	$u+v$	u	v
0	1350	660	690	1140	450	690	1050	360	690
0·0001	1335	654	681	1129	448	681	1037	356	681
0·001	1313	643	670	1110	440	670	1013	343	670
0·01	1263	619	644	1059	415	644	962	318	644
0·03	1218	597	621	1013	390	623	917	298	619
0·1	1153	564	589	952	360	592	853	259	594
0·3	1088	531	557	876	324	552	774	217	557
1·0	1011	491	520	765	278	487	651	169	482
3·0	911	442	469	582	206	376	463	115	348
5·0	—	—	—	438	153	285	334	80	254
10·0	—	—	—	—	—	—	117	25	92

[1] *Wied. Ann.* 1893, 50, p. 385.

This fact enabled Kohlrausch to assign specific ionic velocities to many ions—velocities which depended only on the ion and the solvent through which it was travelling, and were independent of the nature of the other ion present. A list of Kohlrausch's latest values for these is given below. It shews the velocities with which the ions move through an infinitely dilute aqueous solution at 18° C, under a potential gradient of one volt per centimetre.

	cms.			cms.
K	66×10^{-5} per sec.		Cl	69×10^{-5} per sec.
Na	45	,, ,,	I	69 ,, ,,
Li	36	,, ,,	NO_3	64 ,, ,,
NH_4	66	,, ,,	OH	182 ,, ,,
H	320	,, ,,	$C_2H_3O_2$	36 ,, ,,
Ag	57	,, ,,	$C_3H_5O_2$	33 ,, ,,

It is interesting to calculate the magnitude of the forces required to drive the ions with a certain velocity. If we have a potential gradient of one volt per centimetre, the electric force is 10^8 in C.G.S. units. The charge of electricity on one gram-equivalent of any ion is $1/\cdot0001035 = 9653$ units, hence the mechanical force acting on this mass is 9653×10^8 dynes. This, let us say, produces a velocity u, then the force required to produce unit velocity is

$$P_A = \frac{9\cdot653 \times 10^{11}}{u} \text{ dynes} = \frac{9\cdot84 \times 10^5}{u} \text{ kilograms-weight.}$$

If the ion have an equivalent weight A, the force producing unit velocity when acting on one gram is

$$P_1 = 9\cdot84 \times \frac{10^5}{Au} \text{ kilograms-weight.}$$

Thus, in order to drive one gram of potassium ions with a velocity of one centimetre per second through a very dilute solution, we must exert a force equal to the weight of 38 million kilograms.

	Kilograms Weight			Kilograms Weight	
	P_A	P_1		P_A	P_1
K	15×10^8	38×10^6	Cl	14×10^8	40×10^6
Na	22 „	95 „	I	14 „	11 „
Li	27 „	390 „	NO_3	15 „	25 „
NH_4	15 „	83 „	OH	5·4 „	32 „
H	3·1 „	310 „	$C_2H_3O_2$	27 „	46 „
Ag	17 „	16 „	$C_3H_5O_2$	30 „	41 „

Since the ions move with uniform velocity, the frictional forces brought into play must be equal and opposite to the driving forces acting, and therefore these numbers also represent the ionic friction coefficients in very dilute solution at 18° C.

From a table of ionic velocities, we can, by the help of equation (26), calculate the molecular conductivity of any given solution, and the agreement with observation of numbers so deduced gave the first confirmation of Kohlrausch's theory. Instead of using the ionic velocities deduced from the limiting values of the molecular conductivities, we can calculate them for solutions of finite strength, and as long as the solutions are fairly dilute, the numbers so obtained for any one ion, though less than the limiting values, will still be sensibly the same for all solutions containing that ion. We can then calculate the conductivity of any given solution of the same concen-

tration and compare the result with observation. Thus Kohlrausch gives a table of velocities of ions in solutions containing one tenth gram-equivalent of electrolyte per litre, and then calculates the conductivity of different solutions of that strength containing those ions. The numbers all agree with observation for well conducting solutions like those of mineral salts and acids, but in the case of substances whose molecular conductivity varies greatly between a strength of one tenth gram-equivalent per litre and infinite dilution, the effect of concentration is so great that no agreement is obtained; thus acetic acid should give a value of 3168×10^{-13}, while the observed number is 46×10^{-13} for this strength, and only rises to 1386×10^{-13} for a strength of one hundred thousandth of a gram-equivalent per litre.

If we examine Kohlrausch's theory in order to find some explanation of this discrepancy, it appears that it could be due to one of two causes. Either the velocities of the ions must be much less in these solutions than in others, or else only a fractional part of the number of molecules present can be actively concerned in conveying the current. We shall return to this point later.

The first direct experimental determination of the speed of an ion was made by Oliver Lodge[1]. A horizontal glass tube was filled with agar-agar jelly, in which sodium chloride was dissolved, with just enough caustic soda added to make it alkaline and bring out the red colour of a little phenol-phthallein. The ends of the tube were immersed in two vessels containing dilute sulphuric acid.

[1] *B. A. Report*, 1886, p. 393.

A current of electricity was then passed from one vessel to the other through the tube. The hydrogen ions of the sulphuric acid travel with the current, and when they enter the tube, displace the sodium ions, which are also moving in the same direction, and form hydrochloric acid. This decolourises the phenol-phthallein, and thus the motion of the hydrogen along the tube can be traced. Lodge found, as the results of three experiments, that the velocity of the hydrogen ion came out 0·0029, 0·0026 and 0·0024 cms. per second, under a potential gradient of one volt per centimetre. If these numbers are compared with Kohlrausch's calculated values 0·0032 for infinite dilution, or 0·0028 for a decinormal solution, it will at once be seen how striking the agreement is.

The present writer[1] has determined the velocity of a few other ions by another method. Suppose we have two solutions like copper chloride and ammonium chloride, containing one ion in common, and having nearly equal conductivities. Let one solution be coloured, and have a density different from that of the other. The denser solution is first poured into the longer arm of a kind of U tube (see fig. 16), and then the other is allowed to flow gently on to its surface from the shorter arm. If a current is passed across the junction between the two solutions, it carries the copper and ammonium ions with it, and drives the chlorine ions in

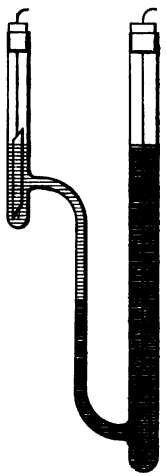


Fig. 16.

[1] *Phil. Trans.*, 1893, A. p. 337.

the opposite direction. Since the colour depends on the presence of the copper ions, the boundary will travel with the current, and, by measuring its velocity, the speed of the ions under unit potential gradient can be calculated. The specific ionic velocities of copper and of the anion of potassium bichromate (the group Cr_2O_7), determined in this way, were found to agree with the values deduced from Kohlrausch's theory. Measurements were also made with alcoholic solutions, the conductivities of which are much less than those of aqueous solutions of corresponding strength, and again a satisfactory agreement with theory was observed. The velocity of the hydrogen ion through sodium acetate has also been determined by a modification of Lodge's method[1]. In this case the hydrogen ion forms acetic acid as it travels, and it was found that, when travelling through a solution of sodium acetate in agar jelly of strength 0·07 gram-equivalent per litre, its ionic velocity was about 0·000065 cms. per second. This great reduction in the speed of hydrogen shews that *the ionic velocities are reduced in these abnormal cases in about the same ratio as the conductivity.* Our equation on p. 136 will therefore always give the conductivity of any solution, if we know the proper values to assign to the velocities of the ions.

[1] *Phil. Mag.* 1894, 2, p. 392.

CHAPTER IX.

ELECTRICAL PROPERTIES (*continued*).

52. Resistance of Electrolytes. The investigation of the laws which govern the passage of currents through electrolytes, and of the relation between current and electromotive force, offers some difficulties owing to the phenomena of polarisation. In the case of metallic conductors, it is found that the current produced is proportional to the electromotive force applied, and is given by $i = E/R$ where R is a constant for any given conductor under fixed conditions, called its resistance. This is Ohm's law, which is proved by shewing that the measured resistance of a conductor is independent of the strength of the current passing through it. Now we have seen that no permanent current will flow through an electrolytic cell unless the electromotive force applied exceeds a certain critical value, so that it appears at first sight that Ohm's law cannot hold. But, in order to apply the law, we must consider the effective electromotive force acting round the circuit, which is equal to the difference between the external applied electromotive

force and the reverse electromotive force due to the polarisation of the electrodes. When this is done, Ohm's law is found to still hold good.

53. Experimental Methods. Many attempts were made to measure the resistances of electrolytes before a satisfactory method was discovered. Horsford[1] passed a current between two electrodes in a rectangular trough, then moved them nearer together, and determined the resistance of a wire which, when interposed in the circuit, reduced the current to its former value. Assuming that the polarisation is the same in the two cases (which, owing to migration, is difficult to insure) the resistance of the wire is the same as that of a column of solution equal in length to the difference of the distances between the electrodes in the two positions. The method was improved by Wiedemann, who used as electrodes plates of the metal present in solution, and thus reduced polarisation.

Beetz[2] used an ordinary Wheatstone bridge arrangement, getting rid of nearly all polarization by making his electrodes of amalgamated zinc placed in a neutral solution of zinc sulphate.

Since the electromotive force between any two points of a given circuit is proportional to the resistance between them, the resistance of two parts of a circuit can be compared by comparing the electromotive forces between their ends. In this way Bouty[3] examined many solutions; he placed them in the inverted U tubes

[1] *Pogg. Ann.*, 1847, 70, p. 238. [2] *Pogg. Ann.*, 1862, 117, p. 1.
[3] *Ann. de Chemie et de Physique* 1884, iii.

a and b (fig. 17), the legs of which dipped in larger volumes of the same solutions placed in porous pots. These porous pots were immersed in larger cells filled with zinc sulphate solution, and connections were made with siphons

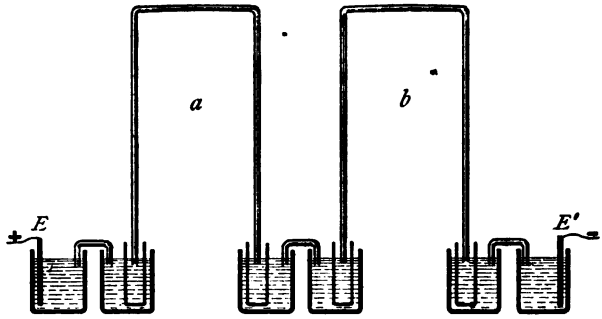


Fig. 17.

filled with the same liquid, as shewn in the diagram. The main electrodes E and E' were of amalgamated zinc, and a current was passed between them. Two tapping electrodes were constructed, each consisting of a zinc rod in sulphate of zinc solution placed in a Woulffe's bottle, with a thin siphon tube coming out of one neck to make connection with the liquid in either of the cells. In this way the electromotive forces between the ends of a and b were compared. The only polarisation is at the contact of the different solutions outside and inside the porous pots.

The best measurements of the resistances of electrolytes hitherto made are due to Kohlrausch[1]. In order to avoid the effects of polarisation, alternating currents (that is currents whose direction is constantly being re-

[1] *Pogg. Ann.*, 1869, 138, pp. 280, 370; 1873, 148, p. 143; & 1874, J. p. 290.

versed) are used. The electromotive force of polarisation is thus rapidly reversed, and never reaches its full magnitude. Still, unless proper precautions are taken, polarisation is produced by such a small amount of chemical decomposition that, even with alternating currents, its effect is important, and the resistance as measured is found to depend on the rate of alternation. It was found that the products of the decomposition of $\frac{1}{70}$ milligram of water on two platinum plates, each having an area of one square metre, gave an electromotive force of about one volt, and that the electromotive force of polarisation was proportional to the surface density of the deposit: it can therefore be made as small as we please by increasing the area of the electrodes. The effective area can be made much larger by coating the electrodes with platinum-black. This is done by passing a current backwards and forwards between them through a dilute solution of platinum chloride containing free nitric acid.

It has been usual to employ the alternating currents given by a small induction coil, and to adjust a Wheatstone's bridge till the sound given by the telephone, used as indicator, was a minimum. Various disturbing causes must, however, in that case, be taken into account or eliminated. Thus the self-induction of the circuit produces an effect. This is opposite to that of polarisation, and, by proper adjustments, can be made to balance it[1]. The electrostatic capacity of the apparatus is also of importance[2].

[1] *Enc. Brit.*, Art. "Electricity," or *B. A. Report*, 1886, p. 384.

[2] See Chaperon, *Compt. Rend.* 1889, 108, p. 799, and Kohlrausch, *Zeits. f. physikal. Chem.* 1894, 15, p. 126.

A modification of the method, described by Fitzpatrick[1] and now in constant use at Cambridge, eliminates all such periodic disturbances. The current from one or two Leclanché cells is led to an ebonite drum, which is kept revolving at a very uniform rate by means of a turbine. This is driven by a water supply carefully kept at constant pressure. On the drum are fixed brass sectors, with wire brushes touching them in such a manner that the current is reversed several times in each revolution. The wires from the drum are then led to an ordinary resistance box, and connected in the same way as the battery wires of a Wheatstone's bridge. A reflecting galvanometer is used as indicator, and, on the back of the drum, there is another set of sectors, arranged to periodically reverse the galvanometer connections, so that any residual current always flows through it in the same direction. These sectors are rather narrower than the others, so that the galvanometer circuit is made just after the battery circuit is made, and broken just before the battery circuit is broken. The needle of the galvanometer is loaded with lead; its moment of inertia is therefore considerable, and its period of vibration very long compared with the period of alternation of the current. This prevents the slight residual effects of polarisation, and of other periodic disturbing causes, from sensibly affecting the galvanometer. When the measured resistance keeps the same on increasing the speed of the turbine and changing the ratio of the arms of the bridge, the disturbing effects may be considered to be eliminated.

[1] *B. A. Report*, 1886, p. 328.

Various shaped vessels are used to contain the electrolytes; a convenient form is represented in fig. 18. A glass

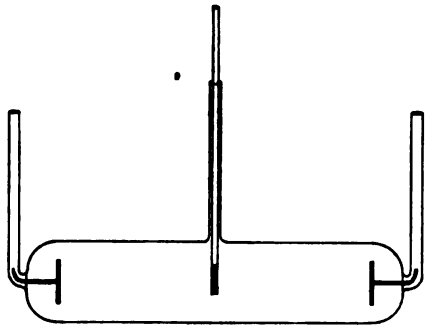


Fig. 18.

tube, about an inch or an inch and a half in diameter, has a tube sealed in at one side through which a thermometer can be inserted, and a stout platinum wire carrying a platinum plate sealed through each end. Little tubes to hold mercury are fixed over the protruding ends of these wires, and, in this way, connection is easily made with the Wheatstone's bridge. The constant of the cell is determined once for all by measuring in it the resistance of a standard solution. From the observed resistance of any solution in the cell, we can then calculate the resistance of a centimetre cube, which is called the *specific resistance*. The reciprocal of this, the *specific conductivity*, is a more generally useful constant. As the temperature coefficient is large (it is about two per cent. per degree for moderately dilute aqueous solutions of common salts or acids), it is necessary to keep the cell in a paraffin bath, and observe the temperature with some accuracy.

54. Experimental Results. Kohlrausch expressed his results in terms of molecular conductivity, that is the conductivity (k) divided by the number of gram-equivalents of electrolyte per litre (n). He finds, that, as the concentration diminishes, the value of k/n approaches a limit, and, if the dilution is pushed far enough, becomes constant, that is to say, that at great dilution the conductivity is proportional to the concentration. Kohlrausch established this by preparing very pure water by careful distillation. He found that the resistance of the water continually increased as the process of purification proceeded. The conductivity of the water, and of the slight impurities which must always remain, was subtracted from that of the solution, and the result, divided by n, gave the molecular conductivity of the substance dissolved. This appears justifiable, for, as long as conductivity is proportional to concentration, it is evident that each part of the dissolved matter produces its own independent effect, so that the total conductivity is the sum of those of the parts, and when this ceases to hold, the conductivity of the solution has, in general, become so great that that of the solvent is negligible.

The general result of these experiments can be graphically represented by plotting k/n as ordinates, and $n^{\frac{1}{3}}$ as abscissæ; $n^{\frac{1}{3}}$ is a number proportional to the reciprocal of the average distance between the molecules—to which it seems likely that the molecular conductivity will be closely related. The general form of the curves for a neutral salt, and for a caustic alkali or univalent acid (like HCl) are shewn in fig. 19. The curve for

the neutral salt comes to a limiting value, while that for the acid attains a maximum at a certain (very small) concentration, but when the dilution is pushed to extreme limits, it falls again. This Kohlrausch considered to be due to chemical action between the acid

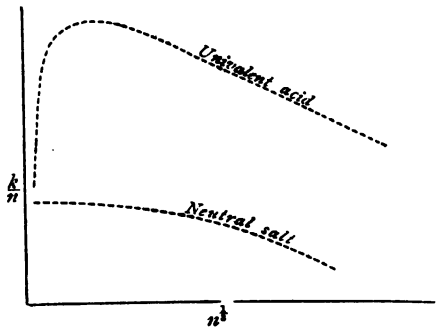


Fig. 19.

and the residual impurities in the water, which, at such great dilution, are present in quantities quite comparable with the amount of acid. He therefore considered the maximum value to be the limit in the case of acids. It will be seen from our tables in the appendix that the values of the molecular conductivities of all neutral salts are, at great dilution, of the same order of magnitude, while those of acids at the maximum are about three times as great. The influence of increasing concentration is greater in the case of salts containing divalent ions than for those composed only of univalent ions, and greatest of all in such cases as ammonia and acetic acid, which hardly conduct any better in strong solutions than in weak.

The most important results of Kohlrausch's work are—

1. The proof of Ohm's law for electrolytes.

2. The fact that the conductivity of dilute solutions can be represented as the sum of two independent factors, each of which depends on one of the ions only, and the consequent possibility of determining the ionic velocities by the method described in Chapter VIII.

55. Consequences of Ohm's Law. A direct proof of Ohm's law for electrolytes has also been given by Fitzgerald and Trouton[1], who shewed that the measured resistance was independent of the strength of the current. The agreement with the law is a fact of great interest. Since any electromotive force, even if very small, must be able to produce a corresponding current, there can be no appreciable reverse electromotive forces in the interior of an electrolyte, and no appreciable amount of chemical work can be there done by the current. It follows either that the function of the current is merely directive—that it controls the direction of the motions of the ions which it already finds continually interchanging their partners—or else that the work done in tearing one molecule asunder is exactly equal to that given back in the formation of the next.

The first of these hypotheses was advanced by Clausius[2] to explain the facts of electrolysis, and, as it is the one generally adopted, we will examine the evidence for it in some detail. If two solutions containing the salts

[1] *B. A. Report*, 1886, p. 312.

[2] *Pogg. Ann.*, 1857, 101, p. 338.

AB and CD are mixed, double decomposition is found to occur—AD and CB being formed. This goes on till a certain part of the first pair of substances has been transformed into an equivalent amount of the second pair. The proportions between the four salts AB, CD, AD and CB, which finally exist in solution, are found to be the same whether we begin with AB and CD or with AD and CB. The phenomena were found by Guldberg and Waage to be fully represented by a theory which supposed that both the change from AB and CD into AD and CB, and the reverse change from AD and CB to AB and CD were always going on, the quantities transformed per second being proportional to the product of the active masses of the original substances and to a coefficient k, which expresses the affinity producing the reaction. If the active masses of AB, CD, AD, CB are p, q, p', q' respectively, and k and k' the two coefficients of affinity, we get for the rate of transformation of AB and CD into AD and CB

$$kpq,$$

and for the velocity of the reverse change

$$k'p'q'.$$

When there is equilibrium, these two rates of transformation must be equal and opposite, and we get

$$kpq = k'p'q' \ldots\ldots\ldots\ldots\ldots\ldots (27).$$

The results of this equation have been experimentally confirmed for many cases, and the view here taken of double decomposition is universally admitted to be a true one. But in order that this process of chemical change

in opposite directions should continually go on, it is obviously necessary that perfect freedom of interchange should exist between the parts of the molecules, so that, here again, we are forced to believe that a series of perpetual separations and reunions is going on among them. This hypothesis was first advanced from the chemical side by Williamson[1] in order to explain the process of etherification.

A study of chemical changes shews us that it is always the electrolytic ions of a salt that are concerned in the reactions. The tests for a salt, potassium nitrate for example, are the tests not for KNO_3, but for its ions K and NO_3, and in cases of double decomposition, it is always these ions that it exchanges for those of other substances. That this is the case is shewn by the fact that, if an element is present in a compound otherwise than as an ion, it is not interchangeable, and cannot be recognised by the usual tests. Thus neither the chlorates, which contain the ion ClO_3, nor monochloracetic acid, shew the reactions of chlorine, although of course it is present in both; and the sulphates do not answer to the usual tests which indicate the presence of sulphur as sulphide.

It seems certain, then, that the parts of the molecules in solution are continually changing partners, that the electrolytic ions are also the parts which enter into chemical combinations, and that the effect of a current is merely so to control the direction of these decompositions and recompositions, that, on the whole, a stream of positively electrified ions travels in one direction, and

[1] *Chem. Soc. Journal*, 1852, 4, 110.

a stream of negatively electrified ions in the other. As far as we have gone, there is no evidence to shew that the ions remain dissociated for any appreciable time, the reasoning given above only goes to prove that there is freedom of interchange. This freedom may only exist in the case of those molecules which the kinetic theory teaches us will, at any instant, happen to be moving with a velocity so much greater than the average, that, on colliding with another molecule, the impact is violent enough to produce dissociation, and make rearrangement possible. So much seems to follow from the truth of Ohm's law and the phenomena of chemical action. There is further evidence, which we shall discuss later (see Chap. XI.), that the ions remain dissociated, or at all events keep a certain amount of freedom, throughout a considerable fractional part of their existence.

56. Influence of Concentration on Conductivity. The tables given in the appendix shew at once that the molecular conductivity of solutions falls off as the concentration increases, that is to say, the conductivity does not increase as fast as the concentration, so that the effect of each successive increase in the amount of salt dissolved becomes less. How are we to explain this? It follows from the experimental determination of the velocity of the hydrogen ion in acetic acid solutions, described on page 142, that the *immediate* cause of the reduction in molecular conductivity is a reduction in the velocities of the ions. It is true that the viscosity of a solution increases with the concentration, so that the frictional

resistance to the motion of the ions may become greater, but this is a small change, insufficient to explain the marked decrease in molecular conductivity, and Arrhenius[1] has shewn that, at any rate in many cases, there is no proportionality between viscosity and electrical resistance. We can, however, imagine another way in which the average velocities of the ions might be reduced: viz. by supposing that the ions are only able to move during a part of their time, so that each molecule in solution becomes in turn active and inactive.

57. Dissociation Theory. A theory of electrolysis, which has been framed by Arrhenius, Ostwald and others, supposes that a substance is chemically active only when dissociated, in which state the ions are to some extent free from each other. In the language of this "Dissociation Theory" the freedom of interchange which we know to exist among the ions, is secured, not by the momentary dissociation and consequent rearrangement at the instant of collision of the molecules, as described on page 154, but by the continued freedom of the ions for a considerable part of their existence. Dissociation and recomposition are continually going on, and a substance is active only while its ions are dissociated and able to move. An ion will, at one instant, be combined with another, forming an inactive molecule, at another, be travelling freely through the liquid under the influence of the electric forces, and, at a third, combined with a fresh one of the opposite kind to form a new inactive molecule. Dissociation is

[1] *B. A. Report*, 1886, p. 344.

possibly caused by collisions as Clausius supposed, but Arrhenius says that the ions do not at once recombine with others as the older theory imagined. We shall see later (§ 79) that the forces between atoms are much reduced by solution in a solvent of high specific inductive capacity, which will give greater freedom, and that there is some reason to suppose that the ions, when free from each other, are combined with the solvent molecules, which pass them on from one to the other through the liquid.

58. Ionisation. The dissociation theory will be considered in greater detail later, it is only introduced here to give some idea of how ions can be in turn active and inactive. But though the most obvious, it is not the only way in which such a result could be secured. The activity of a molecule might be due to a particular arrangement of complex structures formed with other molecules, either of the substance dissolved or of the solvent, in which state alone transference of ions could occur, or it might be that the contact of two molecules in a particular position was the necessary condition for interchange of their ions. In either of these ways it could be managed that a part only of the dissolved substance should be at any moment in a state of electrolytic activity, which is all that is necessary to produce the diminution of ionic velocity which we require. Instead of using the word "dissociation" to express the active state of a molecule, we shall use, at Fitzgerald's suggestion[1], the term "ionisation." Even if the process of ionisation does consist in giving a certain

[1] *B. A. Report*, 1890, p. 142.

amount of freedom from chemical chains to the parts of a molecule, it is certain that the ions so produced are not in the same electrical or chemical state as the elements would be if they were dissociated from each other by ordinary chemical processes, and it would be better to restrict the term "dissociation" to such cases as the resolution by heat of solid ammonium chloride into gaseous ammonia and hydrochloric acid.

59. Influence of Concentration on Ionisation. We have now found a way in which the ionic velocities, and consequently the molecular conductivity, of a solution may be reduced, and we can, therefore, return to the consideration of the effect of increasing concentration. In the normal case, in which the molecular conductivity tends to a limiting value at great dilution, we can suppose we have got all the contents of the solution in a state of activity. As the concentration increases, and the molecular conductivity gets less, the proportion of active molecules continually decreases, so that the ratio of the number of active to the whole number of molecules is the same as the ratio of the molecular conductivity at the given concentration to that at infinite dilution. This ratio (α) can be called the coefficient of ionisation, and its value, for any given solution, is

$$\alpha = \frac{\mu}{\mu_\infty},$$

where μ represents the molecular conductivity of the solution, and μ_∞ its value at infinite dilution. The following table gives Kohlrausch's results for a solution of potassium chloride.

n	$\mu \times 10^6$	a
0·0	1296	1·00
·0001	1285	·99
·0006	1275	·98
·001	1268	·98
·006	1235	·95
·01	1219	·94
·03	1178	·90
·1	1113	·86
·5	1018	·78
1·0	977	·75
3·0	879	·68

60. Resistance of Liquid Films. Reinold and Rücker[1] have investigated the electrical resistance of thin soap films. By examining the effect on interference phenomena of passing one of the interfering rays of light through a tube across which several films were stretched, they were able to measure the thickness of the films with considerable accuracy. This method assumes that the index of refraction of a film is the same as that of the liquid in bulk, but reasons are given to justify this assumption. It was found that, when films were prepared which, like the central spot of Newton's rings, looked black by reflected light, the thickness was constant for any given liquid. If some salt was added to the liquid, the thickness decreased; thus the following table shews the thickness in micro-millimetres (metre $\times 10^{-10}$), of films of 1 part of hard soap in 40 parts of water with varying amounts of potassium nitrate.

[1] *Phil. Trans.*, 1893, 1, p. 505.

Optical Method.

Percentage of KNO_3	3	1	0·5	0
Thickness in $\mu\mu$	12·4	13·5	14·5	32·1

If the specific resistance of the film is the same as that of the liquid in bulk, we ought to be able, by measuring the resistance of a film of known size, to get values for the thickness, agreeing with these numbers. It was found that, as long as the amount of salt present was greater than 3 per cent., the results of the two methods agreed, but if the proportion was less than this, the electrical method gave a greater value than the optical.

Electrical Method.

Percentage of KNO_3	3	2	1	0·5	0
Thickness in $\mu\mu$	10·6	12·7	24·4	26·5	154

Thus the conductivity of a thin film is much greater than that of the liquid in bulk when the concentration is very small, but, as the concentration increases, the conductivity more and more nearly approaches the normal value, which it reaches when the strength of solution is about two or three per cent.

We cannot explain this phenomenon by supposing that the surface tension increases the ionisation, because it is in the case of very dilute solutions, where the ionisation is already nearly complete, that the effect is most marked. The ionic friction may, however, be less, and the ionic velocities greater, in the surface layer than in the bulk of the liquid.

61. Electrical Endosmose. If we pass an electric current through a cell divided into two compartments by

means of a porous partition and filled with some solution, we shall, in general, find that, as well as alterations in the contents of the solutions round the electrodes, there is a bodily transfer of the liquid—usually in the direction of the current—through the porous plate. To this phenomenon the name of electric endosmose is given. It has been experimentally studied by Wiedemann[1] and Quincke[2]. If the pressure be kept the same on both sides of the partition, the volume of liquid which flows through, as measured by the overflow, is proportional to the whole quantity of electricity which has passed, and is independent of the area and thickness of the porous plate; it varies much with the nature of the solution, being greater with liquids of high specific resistance, and, in solutions of any one substance of different strengths, is approximately proportional to the specific resistance.

If we do not allow the liquid to overflow, but measure the final pressure reached, we find that this pressure varies directly as the strength of the current, inversely as the area of the porous wall, and directly as its thickness. In this case, the flux of liquid due to the electric forces must be equal and in the opposite direction to that caused by the difference in hydrostatic pressure.

A mathematical theory of the subject has been given by von Helmholtz[3], on Quincke's assumption of a constant difference in potential at the surface of contact between the liquid and the walls of the little tubes which run through the porous partition.

[1] See *Elektricität*, Bd. II., p. 166. [2] *Pogg. Ann.*, 1861, 113, p. 513.
[3] *Wied. Ann.*, 1879, 7, p. 337.

Such a discontinuity in potential must produce an "electrical double layer"—that is a charge of one kind of electricity on the walls of the tube, and an equal charge of the opposite kind on the nearest film of liquid. The latter charge is acted on by the external electric forces, and the liquid is dragged through the tube by its skin. When a difference of pressure is allowed to develop, one current of liquid is dragged forward along the walls, and another flows back down the centre of each little tube, and, when a stationary state is reached, the volumes flowing in these two currents are equal and opposite. From these ideas Helmholtz deduced all the observed laws of electric endosmose, and calculated that the contact differences of potential, which would produce the observed effects, are comparable with the electromotive force of a Daniell's cell. A modification of Helmholtz's theory has been given by Lamb[1] allowing for some slight slip between the liquid and the walls of the tubes.

A similar contact difference of potential will explain the motion of fine particles of clay or other material through water or other liquids under the influence of an external electromotive force. Details of observations on these phenomena will be found in the fourth chapter of the second volume of Wiedemann's "*Elektricität.*"

[1] *B. A. Report*, 1887, p. 495.

CHAPTER X.

CONNECTION BETWEEN ELECTRICAL AND OTHER PROPERTIES.

62. Conductivity and Chemical Activity. It was noticed by Hittorf that there was a very close connection between chemical activity and electrical conductivity, but the exact numerical agreement was first pointed out by Arrhenius[1].

It is found that the constant k, which we have used on p. 152 to express the "affinity" determining the rate of transformation of two compounds AB and CD into AD and CB, and likewise the constant k', which controls the reverse action, can each be considered as the product of two factors, one measuring a characteristic property of each of the reacting bodies. This leads to the idea of "specific coefficients of affinity," which is of the utmost importance in the modern theory of chemistry, and is based on the fact that the relative affinities of different acids are the same, whatever the nature of the action by which they are compared.

By measuring the heat evolved during the action, Thomsen determined how much of the sodium salt of one

[1] "Recherches sur la conductivité galvanique des Électrolytes," Stockholm, 1883. Abstract in *B. A. Report*, 1886, p. 357.

acid was decomposed by another, which gives the ratio in which the base is shared by the acids. Ostwald[1] investigated the relative affinities of acids for potash, soda, and ammonia, and proved them to be independent of the base used. The method employed was to measure the changes in volume caused by the action. His results are given in column I. of the table on p. 164, the affinity of hydrochloric acid being taken as one hundred.

Another method is to allow some acid to act on an insoluble salt, and to measure the quantity which goes into solution. Determinations have been made with calcium oxalate $CaC_2O_4 + H_2O$, which is easily decomposed by acids, oxalic acid and a soluble calcium salt being formed. The affinities of acids relative to that of oxalic acid are thus found, so that the acids can be compared among themselves. Their relative affinities as thus measured are given in column II. of the table.

If an aqueous solution of methyl acetate is allowed to stand, a very slow decomposition into alcohol and acid goes on. This is much quickened by the presence of a little dilute acid, though the acid remains unchanged. It is found that the influences of different acids on this action are proportional to their specific coefficients of affinity. The results of this method are given in column III.

Finally in column IV. the electrical conductivities of normal solutions of the acids have been tabulated. A better basis of comparison would be the ratio of the actual to the limiting conductivity, but, since the conductivity

[1] *Lehrbuch der Allg. Chemie.*

of acids is chiefly due to the hydrogen, its limiting value is nearly the same for all, and the general result of the comparison would be unchanged.

The fact, which we have already noticed, that the electrolytic conductivity of solutions of mineral acids attains a maximum value, shewing that the ionisation is complete, corresponds to the phenomena observed in the case of their chemical affinities. The value of these for hydrochloric, nitric and other strong acids is practically the same, and cannot by any means be increased. Thus Ostwald has found that the introduction of oxygen, sulphur or a halogen, which increases the affinity of a weak acid (compare acetic acid with the three chloracetic acids), has no effect on the affinity of these strong acids. The limit has evidently been reached, and the whole substance obtained in a state of activity. In each column of the following table the number for hydrochloric acid has therefore been made equal to 100.

Acid	I	II	III	IV
Hydrochloric	100	100	100	100
Nitric	102	110	92	99·6
Sulphuric	68	67	74	65·1
Formic	4·0	2·5	1·3	1·7
Acetic	1·2	1·0	0·3	0·4
Propionic	1·1		0·3	0·3
Monochloracetic	7·2	5·1	4·3	4·9
Dichloracetic	34	18	23·0	25·3
Trichloracetic	82	63	68·2	62·3
Malic	3·0	5·0	1·2	1·3
Tartaric	5·3	6·3	2·3	2·3
Succinic	0·1	0·2	0·5	0·6

It must be remembered that, the solutions not being of quite the same strength, these numbers are not strictly comparable, and that the experimental difficulties involved in the chemical measurements are considerable. Nevertheless, the remarkable general agreement of the numbers in the four columns is quite enough to shew the intimate connection between chemical activity and electrical conductivity. We may take it, then, that only that portion of a body is chemically active which is electrolytically active—that ionisation is necessary for chemical activity just as it is necessary for electrolytic conductivity.

63. Conductivity and Osmotic Pressure. During our examination of the phenomena of osmotic pressure and its consequences—the lowering of vapour pressure, and the depression of the freezing point—we noticed that the values for solutions of electrolytes were in all cases abnormally great. As more investigations have been made on the depression of the freezing point than on the other correlated properties, and as the experimental error is probably less in this case, we shall at first confine ourselves to it. In order to shew the intimate relation which exists between the abnormal osmotic pressures, as measured by the depression of the freezing point, and the electrical conductivity, we must suppose that every electrolytically active molecule produces an abnormally great osmotic pressure, and that its effect is proportional to the number of ions into which it can be resolved. Thus the effect of an active molecule of KCl is twice that of an inactive one, and the effect of a molecule

of H_2SO_4 (which gives two H ions and one SO_4 ion) is, when in a state of ionisation, three times as great as that of the normal. If then, in a certain solution, we have m inactive and n active molecules, each of the latter giving k ions, the total osmotic pressure produced will be proportional to $m + kn$, whereas the normal osmotic pressure would be proportional to $m + n$. By measuring the conductivity we can (see p. 157) find the fractional number of molecules which is at any moment active. Let us call it α.

Now $$\alpha = \frac{n}{m+n},$$

so that, if the ratio of the actual osmotic pressure to the normal is called i,

$$i = \frac{m+kn}{m+n} = 1 + (k-1)\alpha \ldots\ldots\ldots\ldots (28).$$

This same ratio can also be found by direct experiment on the depression of the freezing point, for by Van 't Hoff's equation (14 on p. 57) we know the normal value, and if t be the observed depression for a solution of one gram-equivalent per litre,

$$i = \frac{t}{1{\cdot}89}.$$

We can thus compare the value of i as directly determined by observations on the freezing point, with its value as calculated from the conductivity. The following table is part of that given by Arrhenius[1] for aqueous solutions.

[1] *Zeits. für physikal. Chemie*, 1887, ii., p. 491.

Substance dissolved	No. of gram-equivalents per litre	i observed from freezing points	i calculated from conductivities	α coefficient of ionisation
A. *Non-Conductors.*				
Methyl alcohol CH_3OH	0·1	0·97		
	0·485	0·96		
	0·97	1·00		
Ethyl alcohol C_2H_5OH	0·125	0·97		
	0·62	1·01		
	1·24	1·05		
Phenol $C_6H_5.OH$	0·101	0·96		
	0·216	0·96	1·00	0
	0·558	0·93		
Cane sugar $C_{12}H_{22}O_{11}$	0·00234	1·267[1]		
	0·0445	1·08		
	0·0947	1·11		
	0·316	1·12		
	0·809	1·34		
	1·01	1·43		
B. *Electrolytes.*				
Lithium hydrate LiOH	0·127	1·98	1·90	·90
	0·317	1·89	1·86	·86
Acetic acid CH_3COOH	0·135	1·05	1·01	·01
	0·337	1·04	1·01	·01
	0·842	1·01	1·00	·00
Phosphoric acid H_3PO_4	0·077	1·38	1·32	·11
	0·146	1·27	1·25	·08
	0·319	1·22	1·20	·07
Sodium chloride NaCl	0·0467	2·00	1·88	·88
	0·117	1·93	1·84	·84
	0·194	1·87	1·82	·82
	0·539	1·85	1·74	·74
Silver nitrate $AgNO_3$	0·056	2·02	1·86	·86
	0·140	1·90	1·81	·81
	0·341	1·77	1·73	·73
Potassium sulphate K_2SO_4	0·0364	2·68	2·45	·72
	0·091	2·35	2·33	·66
	0·227	2·21	2·18	·59
	0·455	2·04	2·06	·53
Calcium chloride $CaCl_2$	0·0476	2·74	2·52	·76
	0·119	2·62	2·42	·71
	0·199	2·66	2·34	·67
	0·331	2·73	2·24	·62
Copper sulphate	0·0393	1·33	1·41	·41
	0·112	1·15	1·34	·34
	0·254	1·03	1·27	·27
	0·523	0·94	1·22	·22
	0·973	0·92	1·18	·18

[1] Jones. *Zeits. für physikal. Chemie*, 1893, 12, p. 642.

Another way of tracing the connection between the two effects is to compare the coefficient of ionisation calculated from the depression of the freezing point with its value as found from the conductivity. The following table is given by H. C. Jones[1].

Substance	Concentration in gram-molecules per litre	Coefficient of Ionisation	
		Kohlrausch's result from conductivity	Jones' result from depression of freezing point
HCl ($\mu_\infty = 3455$)	0·002	1·00	0·984
	0·01	0·989	·958
	0·1	0·939	·886
H_2SO_4 ($\mu_\infty = 3342$)	0·003	0·898	·860
	0·005	0·854	·838
	0·05	0·623	·607
HNO_3 ($\mu_\infty = 3448$)	0·002	1·00	·984
	0·01	0·985	·968
	0·1	0·935	·878
H_3PO_4 ($\mu_\infty = 977$)	0·002	0·878	·852
	0·01	0·635	·688
KOH ($\mu_\infty = 2141$)	0·002	1·00	·984
	0·01	0·992	·937
	0·1	0·928	·831
$NaOH$ ($\mu_\infty = 1880$)	0·002	0·989	·984
	·01	0·995	·937
	·05	0·904	·884
NH_4OH ($\mu_\infty = 700$)	0·006	0·166	·111
	·01	0·130	·069
	·05	0·061	·038
K_2CO_3 ($\mu_\infty = 1222$)	0·003	0·920	·966
	·005	0·886	·960
	·05	0·719	·775
Na_2CO_3 ($\mu_\infty = 1746$)	0·003	0·914	·963
	·005	0·860	·959
	·05	0·650	·730

Loomis[2] finds that the molecular depression of the

[1] *Zeits. für physikal. Chemie*, 1893, 12, p. 639.

[2] *Wied. Ann.* 1894, 51, p. 500.

freezing point agrees with that calculated from the conductivity in the case of solutions of sodium chloride, but that solutions of sulphuric acid and magnesium sulphate shew deviations from the theoretical results greater than can be accounted for by experimental errors.

The general agreement between the observed and calculated results is, however, quite enough to shew the intimate connection of the electrical conductivity with the abnormal depression of the freezing point. The cases in which the conductivity is very low, such as solutions of ammonia and acetic acid, are most interesting, for it is in these also that the abnormal increase in the depression of the freezing point is very small. It seems certain that whatever is the cause of the conductivity of electrolytes is also the chief cause of the increase in the osmotic pressure.

CHAPTER XI.

THEORIES OF ELECTROLYSIS.

64. Introduction. In the preceding pages an account has been given of the experimental facts of our subject, and of those theoretical deductions which seem to necessarily follow from them. We have seen that an intimate relation exists between the conductivity of electrolytes and their other physical and chemical properties. The quantitative agreement between the molecular conductivities, the abnormal value of the osmotic pressures, and the specific chemical affinities of electrolytes, certainly shew that the peculiar condition which we have termed "ionisation" is the chief cause of them all. We shall now proceed to examine the theories which have been advanced in order to explain what is the real physical meaning of ionisation, but it should be remarked that no hypothesis advanced merely to explain observed facts, rests on the same sure ground as a theoretical idea which is a necessary consequence of those facts. Nevertheless, a theory, from which deductions can be made agreeing in all respects with the observed phenomena, may continually increase the amount of evidence in its

favour, and, even if it does not represent the actual physical truth, must certainly be based on a deep-seated analogy, so that it cannot fail to throw new light on the subject and point the way for further investigation.

65. The Dissociation Theory. The theory of electrolytes which has been worked out in the greatest detail is certainly that founded by Arrhenius, Kohlrausch, Ostwald and Nernst on Van 't Hoff's view of the nature of solutions. The fact that an indifferent substance exerts in solution the same pressure as in a gaseous state leads, as we have seen, to the idea that the osmotic pressure, like that of a gas, is mainly due, in dilute solutions, to molecular impacts.

It has been noticed already that solutions of salts, acids and alkalies, give greater values for the osmotic pressure and its consequences—the lowering of vapour pressure and the depression of the freezing point—than do the solutions of non-electrolytes. This, it must be noticed, is the case even in dilute solutions, where the intermolecular forces must be small. It seems natural to attempt to explain these abnormal results by an extension of the ideas which have already proved so satisfactory in the normal cases. But, if we again refer the pressure to molecular impacts, we must still suppose that each molecule produces the same effect as before, so that, in the case of electrolytes, we must have in solution a number of effective pressure-producing particles greater than that indicated by the concentration. If we follow this line of argument, we are brought to the idea that a

large part of the number of molecules in solution must be dissociated, so that the number of effective particles is increased. Raoult found that, whereas the molecular depression of the freezing point for dilute aqueous solutions of indifferent substances was 18·9, the result for potassium chloride was 33·6. If we are to explain this by means of molecular impacts, we must imagine that about 78 per cent. of the potassium chloride is dissociated into two parts. Substances which, like barium chloride ($BaCl_2$), can dissociate into three parts, give, in general, a depression of the freezing point nearly three times the normal. Thus barium chloride gives 48·6—corresponding to a dissociation of 79 per cent. By examining Raoult's table on page 64, it will be seen that no substance gives a value which exceeds that calculated from complete dissociation by more than an amount so small that it might be due to secondary effects or experimental errors.

Exactly the same phenomenon is found in the case of direct determinations of osmotic pressure, and of the lowering of vapour pressure. Here again, in order to explain the behaviour of electrolytes by the theory of molecular bombardment, we have to imagine a certain part of the molecules to be dissociated. The percentage of dissociation calculated from these effects agrees fairly well, in most cases, with that deduced from the freezing points. Differences occur, especially in stronger solutions, but it must be remembered that the experimental investigation of either of these phenomena presents greater difficulties than the determination of the freezing point. In the direct

measurement of osmotic pressure, besides uncertainties already mentioned, the membrane may not be quite impervious to the salt[1]. This would result in the measured pressure being too low. In the determination of vapour pressure, the temperature is, in general, different from that of the freezing point, and, in the theory of the subject, we have assumed certain relations which are only approximately true.

66. Chemical Properties. When we pass to the consideration of the chemical properties of solutions, we are forced by the facts of double decomposition to admit that interchanges among the parts of the molecules are always going on, so that, at all events, temporary dissociation must occur. It does not of course follow that the parts remain free for any considerable time—but freedom of interchange is certainly necessary.

67. Independent Ionic Velocities. Turning to the electrical phenomena, we are met at the outset by Kohlrausch's law of the independent velocities of the ions. This is not a *proof* that the ions are permanently dissociated, but it is certainly *evidence* in favour of that view in the case of dilute solutions, for, if the motions of the ions were produced by taking advantage of interchanges at the instants of collision, it seems likely that the average velocity of an ion would depend on the nature and, still more, on the number of the other ions present. Since an ion could, on this hypothesis, only take a step forward when the molecule of which it formed part collided with

[1] See Tammann, *Zeits. für physikal. Chemie*, 1892, 9, p. 97.

another molecule, we should expect the velocity with which the ions worked their way through the solution to increase with the concentration, and the conductivity to increase faster than the concentration. The fact, then, that, in dilute solutions of good electrolytes, the conductivity is proportional to the concentration, and the molecular conductivity constant, is evidence in favour of the permanence of the dissociation.

The mutual independence of the ions is also suggested by the observation that, while the properties of the solutions of indifferent substances are determined by the constitution and bear no definite relation to the properties of the components, the properties of the solutions of electrolytes are additive—that is, can be represented as the sum of those of their parts.

68. Densities of Salt Solutions. Valson[1] found that the specific gravities of salt solutions could be calculated from a table of moduli of the elements of the substance dissolved, the modulus for each element being experimentally determined. The relation is better investigated, however, by considering the specific volume instead of its reciprocal the specific gravity, and Groshaus[2] found that the molecular volume of the dissolved salt was, in dilute solution, the sum of two constants, one determined only by the acid and the other only by the base.

The following table gives the volume-change in cubic centimetres for one gram-equivalent of substance in 10 litres of water:

[1] *Compt. rend.* 1874, 73, p. 441.
[2] *Wied. Ann.* 1883, 20, p. 492.

	H	Na	K	NH_4
OH	18	−5·8	3·6	
Cl	18·3	16·6	26·9	37·4
NO_3	29·0	28·0	38·5	48·2
$\frac{1}{2}SO_4$	16·2	6·4	15·7	24·2

Thus the solution of 40 grams of NaOH in 10 litres of water involves a *contraction* of 5·8 c.c., so that the volume of the solution (viz. 9994·2 c.c.) is actually less than the volume of solvent used. With other solvents increases in the *total* volume may occur; thus a mixture of 100 c.c. of alcohol and 100 c.c. of carbon bisulphide occupies a volume of 202 c.c.

Ostwald[1] has measured the volume-changes accompanying the neutralisation of bases by acids, and shewn that, here again, additive relations appear. Normal solutions of strong acids and strong bases give, on neutralisation, a constant volume change, equal to a contraction of 20 c.c. per litre. The subject has been fully discussed by Nicol[2].

69. Colours of Salt Solutions. Similar relations hold good with regard to the colour of a salt solution[3], which is obtained by the superposition of the colours of the ions and the colour of any undissociated salt. Anhydrous cobalt chloride is blue, while in cold aqueous solution all cobalt salts are red. Red, then, is the colour of the cobalt ion, and only appears when the salt is more or less dissociated. If cobalt chloride is dissolved in alcohol, the

[1] *Z. für prakt. Chemie*, 1878, 18, p. 353.
[2] *Phil. Mag.*, 1883–4, 16, p. 121 and 18, p. 179.
[3] Ostwald's *Lehrbuch*.

conductivity is very low, shewing very incomplete ionisation. The colour is, accordingly, the blue of the undissociated salt. If we slowly add water to this solution, the ionisation gradually increases, and the colour changes to purple and then red. If an aqueous solution be boiled with potassium cyanide, it is decolourised, for a cobalticyanide, $K_3Co(CN)_6$, has been formed; the ions of this compound are 3K and $Co(CN)_6$; the free cobalt ions no longer exist, and the solution ceases to respond to the usual tests for cobalt. That the red colour is really due to the ionisation, and not to a hydrate formed between the cobalt salt and the solvent, is indicated by the additive nature of the phenomena, for, like other properties, the colour of non-electrolytes depends on the constitution and is not additive. The use of indicators, which shew the presence of acids or bases by a change in colour, is a phenomenon of similar character. Thus para-nitrophenol is a weak acid, very little dissociated. The addition of an alkali, soda for example, causes the corresponding salt to be formed. This is largely dissociated, and the intensely yellow colour of the ion $C_6H_4NO_2.O$ is at once seen.

We shall see reasons later (see p. 193) for supposing that, in most cases, a rise of temperature reduces the dissociation of a salt in solution, and increases the number of combined molecules—the increase of conductivity being brought about by a still greater reduction in the viscosity which the solution opposes to the motion of the ions. We should expect, therefore, that, on heating a coloured solution, the colour would become more like that of the undissociated salt. Thus anhydrous copper chloride is a

yellow solid, and the combination of this with the blue of the copper ion produces the green colour of the strong solution. On adding water the colour gets more blue, but on heating it goes back to green. Many similar cases will be found described by J. H. Gladstone[1]. If the absorption spectra of salt solutions are examined, the additive character of the colour is well seen, the absorption bands due to each constituent being unaffected by the presence of the other. The transmitted light is therefore composed of all those rays which have been absorbed by neither constituent.

70. Other Properties. Similar additive relations[2] have been traced in the refraction coefficients, which were found by Gladstone to be an additive property for the case of solutions of active—*i.e.* dissociated—salts, in the optical rotatory powers, in the surface tensions, and in the viscosities of salt solutions, while Perkin, from the phenomena of magnetic rotation, considered, without reference to the dissociation theory, that salts were dissociated into acid and base. The thermal capacities are complicated by the fact that a change of temperature causes, in general, a change in the state of dissociation to an amount dependent on the nature of the substance, but, in completely dissociated solutions, the thermal capacity is also an additive property[3].

The following table gives the change in thermal

[1] *Phil. Mag.*, 1857, (4), 14, p. 423.

[2] Ostwald's *Lehrbuch.*

[3] Marignac, *Ann. Chim. et Phys.*, 1876, (5), 8, p. 410.

capacity which 10 litres of water undergo when one gram-equivalent of the substances indicated are dissolved.

	H	Na	K	NH_4
OH	18	−27	−38	
Cl	−28	−16·3	−30	−13
NO_3	−10·7	− 8·7	−16	7
$\frac{1}{2}SO_4$	9	−25	−36	−16

Thus the thermal capacity of a solution of 40 grams of NaOH in 10 litres of water is 9973—less than that of the water alone.

71. General considerations. That substances, which shew great chemical stability when solid, are largely dissociated when dissolved, is at first sight rather a startling statement. We must remember, however, that it is precisely these bodies which shew the greatest amount of chemical activity, that is to say, more readily exchange their ions with those of other molecules. The fact that a solution of potassium chloride does not shew any of the properties of the elements potassium and chlorine, though it has been urged as an objection, is not a conclusive argument against the theory of dissociation, for the ions are certainly under chemical and electrical conditions very different from those under which the elements can exist in their usual forms. Without entering into the still uncertain question as to the exact relation between the ions and the electric changes they carry, we are at least certain that the ion has to give a certain definite charge of electricity (whatever that may exactly mean) to the electrode before it can be liberated from the

solution in a normal chemical state. The amount of energy possessed by an ion must therefore be very different from that belonging to the same quantity of substance when liberated from solution, and there is no reason to suppose that their properties would be identical. Another objection which has been brought forward is that the two ions would diffuse at different rates, and be therefore separable. But, as soon as an ion got separated from the mass of the substance, it is obvious that electric forces would be brought into play tending to draw it back, and these would increase, as more ions wandered away, till they prevented further diffusion. Still, some separation would occur, and a volume of water, in contact with the solution of an electrolyte, is found to take a potential of the same sign as that of the more diffusible ion, leaving the solution to assume a potential corresponding to that of the less diffusible ion. (See p. 197.)

Further evidence is given by the behaviour of semi-permeable membranes. A membrane of copper ferrocyanide can be prepared which will allow potassium chloride in solution to pass through it, but is quite impermeable to barium chloride. Now, on the theory of free ions, some of the chlorine will again pass, since it could do so in the first case, but the electric forces will prevent any considerable separation from taking place. But if we place some substance like copper nitrate on the other side of the membrane, the chlorine ions, which diffuse in one direction, are replaced by nitric acid ions, which diffuse in the other, and this process will continue till we soon find nitrate mixed with the barium chloride, and chloride

mixed with the copper nitrate. The salts cannot have directly reacted with each other, for neither alone can pass through the membrane, but the phenomenon is readily explained on the hypothesis of free ions[1].

72. Development of the Dissociation Theory. The ordinary laws of chemical equilibrium have been applied to the case of the dissociation of a substance into its ions. Let c be the number of molecules which dissociate per second when the number of undissociated molecules in unit volume is unity, then cp is the number when the concentration is p. Recombination can only occur when two ions meet, and since the frequency with which this will happen is proportional to the square of the ionic concentration, we shall get for the number of molecules re-formed in one second

$$c'q^2$$

where q is the number of dissociated molecules in one cubic centimetre. When there is equilibrium

$$cp = c'q^2.$$

If μ be the molecular conductivity, and μ_∞ its value at infinite dilution, the fractional number of molecules dissociated is μ/μ_∞, and the number undissociated $1 - \mu/\mu_\infty$, so that, if V is the volume of the solution containing one gram-molecule of the dissolved substance, we get

$$q = \frac{1}{V}\left(\frac{\mu}{\mu_\infty}\right) \text{ and } p = \frac{1}{V}\left(1 - \frac{\mu}{\mu_\infty}\right),$$

$$\therefore \frac{c}{V}\left(1 - \frac{\mu}{\mu_\infty}\right) = \frac{c'}{V^2} \cdot \frac{\mu^2}{\mu^2_\infty},$$

[1] Ostwald, *B.A. Report*, 1890, p. 332.

$$\therefore \frac{c}{c'} = \frac{\mu^2}{V\mu^2_\infty \left(1 - \frac{\mu}{\mu_\infty}\right)} = \frac{\mu^2}{V\mu_\infty (\mu_\infty - \mu)} \quad \ldots\ldots(29).$$

Let us put $\mu/\mu_\infty = \alpha$; then α, which we have called the coefficient of ionisation (p. 157), measures both the molecular conductivity referred to its limiting value as unity, and also the fractional number of molecules dissociated.

The equation then becomes

$$\frac{\alpha^2}{V(1-\alpha)} = \frac{c}{c'} = \text{constant} = k \quad \ldots\ldots\ldots(30).$$

This should represent the effect of dilution on the molecular conductivity of binary electrolytes, and Ostwald[1] has confirmed it by observation on an enormous number of acids.

Cyanacetic acid.

V	μ	$100\frac{\mu}{\mu_\infty}$	k
16	78·8	21·7	0·00376
32	105·3	29·1	373
64	139·1	38·4	374
128	176·4	48·7	361
256	219·1	60·5	362
512	260·9	72·0	361
1024	297·3	82·1	368

Formic acid	k = ·0000214	Propionic acid	·0000134
Acetic ,,	·0000180	Butyric ,,	·0000149
Monchloracetic ,,	·00155	Isobutyric ,,	·0000144
Dichloracetic ,,	·051	Isovaleric ,,	·0000161
Trichloracetic ,,	1·21	Caproic ,,	·0000145

[1] *Zeits. für physikal. Chemie*, 1888, ii. p. 270; 1889, iii. pp. 170, 241, 369.

The value of k, however, does not keep so satisfactorily constant in the case of strong acids, and, though the experimental error may be rather larger, no good explanation of this discrepancy has yet been given.

If we put α equal to $\frac{1}{2}$ in equation (30), we find that the value of k is $\frac{1}{2V}$. Thus, $2k$ measures the concentration at which the electrolyte is just half dissociated. Ostwald considers that this constant, k, gives the "long sought numerical value of the chemical affinity."

If we choose states of dilution V_1 and V_2 for two different substances, such that the products V_1k_1 and V_2k_2 are equal, then $\frac{\alpha^2}{1-\alpha}$, and therefore α, must be the same for both. If we alter both dilutions in the same ratio, the products V_1k_1 and V_2k_2 are still equal, so that the dilutions at which two substances are dissociated to the same extent are always proportional, whatever the absolute values of the dilution. This was experimentally discovered by Ostwald before he had applied the theory of dissociation to electrolytes.

In the case of substances like ammonia and acetic acid, where the dissociation is small, $1-\alpha$ is nearly equal to unity, and only varies slowly with dilution. The equation then becomes

$$\frac{\alpha^2}{V} = k,$$

or

$$\alpha = \sqrt{Vk} \quad \ldots\ldots\ldots\ldots\ldots\ldots (31),$$

so that the molecular conductivity should be proportional to the square root of the dilution. If we determine α for

a number of solutions of different strength, and use our results to calculate k, the values obtained should be constant. The following table is given by Ostwald for acetic acid:

V	μ	α	k
8	4·34	·0119	·0000180
16	6·10	·0167	179
32	8·65	·0238	182
64	12·09	·0333	179
128	16·99	·0468	179
256	23·82	·0656	180
512	32·20	·0914	180
1024	46·00	·1266	177

V is the number of litres containing one gram-molecule, μ the molecular conductivity (in mercury units), α the ratio of this to the maximum, $\mu_\infty = 364$. This maximum value is calculated from the velocities of the acetic acid ion and of hydrogen, determined by Kohlrausch from the conductivity of sodium acetate and mineral acids.

If we have once determined the constant k for any electrolyte, we can, by the help of the equation, calculate its conductivity for any dilution.

This account of dissociation applies only to substances which yield two ions, but similar expressions can be deduced for other cases. Thus for a body which gives three ions like $BaCl_2$ or H_2SO_4, the frequency with which recombination will occur will be proportional to the cube of the ionic concentration, so that we get for equilibrium

$$cp = c'q^3$$

which leads to the equation

$$\frac{\alpha^3}{V^2(1-\alpha)} = \frac{c}{c'} = k,$$

and if α is small $\alpha = \sqrt[3]{V^2 k}$.

In the case of weak polybasic acids, succinic for example, the dissociation at first obeys the law for monobasic acids, and varies as the square root of the dilution. This shews that the ions are H and HA'' instead of H, H and A''. When about half the molecules are dissociated, some generally begin to give rise to three ions, and the variation with concentration gradually becomes normal. In the case of strongly dissociated bodies the three ions are always produced.

73. Dissociation of Mixed Solutions. Let us consider, for the sake of example, two simple electrolytes containing one ion in common. We get for our equations of equilibrium

$$c_1 \frac{1-\alpha_1}{V_1} = c_1' \frac{\alpha_1}{V_1} \cdot \frac{\alpha_1}{V_1}$$

and

$$c_2 \frac{1-\alpha_2}{V_2} = c_2' \frac{\alpha_2}{V_2} \cdot \frac{\alpha_2}{V_2},$$

where α is the fraction dissociated, and V the volume containing one gram-molecule.

If we mix the two solutions, the volume becomes $V_1 + V_2$. The concentrations of the undecomposed portions become $\frac{1-\alpha_1}{V_1+V_2}$ and $\frac{1-\alpha_2}{V_1+V_2}$. Those of the unlike

ions fall to $\frac{\alpha_1}{V_1+V_2}$ and $\frac{\alpha_2}{V_1+V_2}$, and that of the common ion will be $\frac{\alpha_1+\alpha_2}{V_1+V_2}$. We thus get

$$c_1\frac{1-\alpha_1}{V_1+V_2}=c_1'\frac{\alpha_1}{V_1+V_2}\cdot\frac{\alpha_1+\alpha_2}{V_1+V_2}$$

and

$$c_2\frac{1-\alpha_2}{V_1+V_2}=c_2'\frac{\alpha_2}{V_1+V_2}\cdot\frac{\alpha_1+\alpha_2}{V_1+V_2}.$$

Dividing each of these into the corresponding equation of the upper pair we get

$$\frac{V_1+V_2}{V_1}=\frac{V_1+V_2}{V_1}\cdot\frac{(V_1+V_2)\,\alpha_1}{V_1(\alpha_1+\alpha_2)}$$

and

$$\frac{V_1+V_2}{V_2}=\frac{V_1+V_2}{V_2}\cdot\frac{V_1+V_2}{V_2}\cdot\frac{(V_1+V_2)\,\alpha_2}{V_2(\alpha_1+\alpha_2)}.$$

Dividing the second of these equations by the first we obtain

$$\frac{V_1}{V_2}=\frac{V_1^2}{V_2^2}\cdot\frac{\alpha_2}{\alpha_1},\ \therefore\ \frac{\alpha_1}{\alpha_2}=\frac{V_1}{V_2}\quad\ldots\ldots\ldots\ldots(32),$$

so that, in order that no change in the number of free ions should occur on mixing, the dissociated portions of two electrolytes must be proportional to the dilutions.

The equation can also be written in the form

$$\frac{\alpha_1}{V_1}=\frac{\alpha_2}{V_2}\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots(33),$$

which shews that the concentration of the ions must be the same in both solutions.

The most important application of this principle is to the case of two acids. In order that no change in the states of dissociation should occur on mixing, it is necessary

that the concentration of the hydrogen ions should be the same in both solutions. Such solutions were called by Arrhenius[1] *isohydric.*

Any two solutions, then, will so act on each other when mixed that they become isohydric. Suppose we have one very active acid like hydrochloric, in which dissociation is nearly complete, and another like acetic, in which it is very small. In order that the solutions of these should be isohydric and the concentrations of the hydrogen ions the same, we must have a very large quantity of the feebly dissociated acetic acid, and a very small quantity of the strongly dissociated hydrochloric, and in such proportions alone will equilibrium be possible. This explains the action of a strong acid on the salt of a weak acid. Suppose we act on dilute sodium acetate with dilute hydrochloric acid. Some acetic acid is formed, and this process will go on till the solutions of the two acids are isohydric: that is till the dissociated hydrogen ions are in equilibrium with both. In order that this should hold, we have seen that a considerable quantity of acetic acid must be present, so that a considerable quantity of the salt will be decomposed, the quantity being greater the less the acid is dissociated. This "replacement" of a "weak" acid by a "strong" one, is a matter of common observation in the chemical laboratory.

Nernst[2] has pointed out that it follows from this theory that, when a salt is dissolved in the saturated solution of

[1] Mém. présenté à l'Acad. des Sciences de Suède le 6 Juin, 1883. Account in *B.A. Report*, 1886, p. 357.

[2] *Zeits. für physikal. Chemie*, 1888, iv. p. 372.

another slightly soluble salt, two principles must hold. The quantity of undissociated salt with which the solution is saturated must keep constant, and the product of the numbers of the opposite ions in solution must also keep constant. Thus, if λ_0 and λ_0' be the solubilities of two salts in pure water, λ and λ' their solubilities when both are present together, and α_0, α_0', α, and α' the corresponding values of the dissociation, we get

$$\lambda_0(1-\alpha_0)=\lambda(1-\alpha)$$
$$\lambda_0'(1-\alpha_0')=\lambda'(1-\alpha'),$$

and from the second principle

$$\lambda_0^2\alpha_0^2=\lambda\alpha(\lambda\alpha+\lambda'\alpha')$$
$$\lambda_0'^2\alpha_0'^2=\lambda'\alpha'(\lambda\alpha+\lambda'\alpha').$$

By means of these equations, the dissociation can be calculated from the solubilities, and Noyes and Abbot[1] have found that, in the cases of three slightly soluble salts of thallium, it agrees with the value obtained from the conductivity.

74. General case of Chemical Equilibrium. Suppose we have four solutions of the substances A_1B_1, A_1B_2, A_2B_1 and A_2B_2, so adjusted that solutions containing a common ion are isohydric. Let a, b, c and d be the relative volumes in which, if the four solutions are mixed, no change occurs, and let β, γ, δ and ζ be the undissociated quantities of the four substances. Since we must have, in all cases, equal concentration of the ions, the dissociated quantities can be represented as ha, hb, hc and

[1] *Zeits. für physikal. Chemie*, 1895, xvi. p. 125.

hd. The equations of dissociation of the solutions thus become

$$\frac{\beta}{a} = k_1\left(\frac{ha}{a}\right)^2, \qquad \frac{\gamma}{b} = k_2\left(\frac{hb}{b}\right)^2,$$

$$\frac{\delta}{c} = k_3\left(\frac{hc}{c}\right)^2 \text{ and } \frac{\zeta}{d} = k_4\left(\frac{hd}{d}\right)^2,$$

or $\beta = k_1h^2a$, $\gamma = k_2h^2b$, $\delta = k_3h^2c$ and $\zeta = k_4h^2d$.

If the four volumes are mixed, new equations will hold

$$\frac{\beta}{a+b+c+d} = k_1\frac{h(a+b)(a+c)}{(a+b+c+d)^2} \text{ \&c....}$$

which reduce to the form

$$\beta = \frac{k_1h^2(a^2+ab+ac+bc)}{a+b+c+d},$$

$$\gamma = \frac{k_2h^2(b^2+ab+bd+ad)}{a+b+c+d} \text{ \&c....}$$

Dividing the corresponding equations by each other we get from each pair

$$ad = bc \text{.....(34)},$$

from which we see that the products of the volumes of such pairs of solutions as contain no common ion must be equal to each other.

Now the volumes a, b, c and d are proportional to the active (or dissociated) portions of the four substances present. Hence the values a, b, c and d are equal to α_1p_1, α_2p_2, α_3q_1 and α_4q_2 respectively, where p_1, p_2, q_1

and q_2 represent the total quantities of the four substances present. We thus get from equation (34)

$$\alpha_1 p_1 . \alpha_3 q_1 = \alpha_2 p_2 . \alpha_4 q_2 \quad \ldots\ldots\ldots\ldots\ldots (35).$$

This expression represents Guldberg and Waage's formula for chemical equilibrium, which has been fully confirmed by observation, and also shews that, as Ostwald has observed, the constants k_1 and k_2 in their equation

$$k_1 p_1 q_1 = k_2 p_2 q_2$$

are made up of two factors, each of which depends only on the nature of one substance.

Many observed facts, before inexplicable, follow at once from our equation. Thus the active portion of slightly dissociated acids must be reduced by the presence of their normal salts, which themselves furnish a supply of the same ions. Such mixtures are found to have less activity than the amount of acid in them would possess alone.

75. Thermal phenomena. The theory gives an immediate explanation of Hess' law of thermoneutrality, which expresses the fact that, in general, no heat change occurs when two neutral salt solutions are mixed. Since the salts, both before and after mixture, exist mainly as dissociated ions, it is obvious that large thermal effects can only appear when the state of dissociation of the products is very different from that of the reagents.

Let us now consider the case of the neutralisation of a base by an acid in the light of the dissociation theory. In dilute solution, such substances as hydrochloric acid

and potash are almost completely dissociated, so that, instead of representing the reaction as

$$HCl + KOH = KCl + H_2O,$$

we must write

$$\overset{+}{H} + \overset{-}{Cl} + \overset{+}{K} + \overset{-}{OH} = \overset{+}{K} + \overset{-}{Cl} + H_2O.$$

The ions K and Cl suffer no change, but the hydrogen of the acid and the hydroxyl (OH) of the potash unite to form water, which is only very slightly dissociated. The heat liberated, then, is almost exclusively that produced by the formation of water from its ions. An exactly similar process occurs when any strongly dissociated acid acts on any strongly dissociated base, so that *in all such cases the heat evolution should be approximately the same.* This is fully borne out by the experiments of Thomsen, who found that the heat of neutralisation of one gram-molecule of a strong base by an equivalent quantity of a strong acid was nearly constant, and equal to 13700 or 13800 calories.

In the case of weaker acids, the dissociation of which is less complete, divergences from this constant will occur, for some of their molecules have to be separated into their ions. For instance, sulphuric acid, which, in the fairly strong solutions used by Thomsen, is only about half dissociated, gives a higher value for the heat of neutralisation, so that heat must be evolved when it is resolved into its ions. The heat of formation of a substance from its ions is of course very different from that evolved when it is made from its elements in the usual way, since the energy

associated with an ion is different from that possessed by the atoms of the element in their normal state. The heat of neutralisation of weak acids can be represented, when the resultant salt is highly dissociated, by

$$N = 13500 + A + B,$$

where A and B depend on the states of dissociation of the acid and base respectively.

We can calculate the heat of formation of any substance from its ions by applying the same thermo-dynamical principles as in the case of vapour pressure or osmotic pressure. Suppose we have an electrolyte which dissociates into two ions. We have shewn (p. 180) that the equation of equilibrium is

$$cp = c'q^2$$

where p and q are the concentrations of the undissociated molecules and of the ions respectively. Since the concentrations are proportional to their partial pressures, we get, if p and q represent these pressures,

$$\frac{q^2}{p} = A\,\frac{c}{c'} = \text{constant} = K.$$

We can now apply the thermo-dynamical equation (2) already used on p. 33. It here takes the form

$$\frac{d\log_e K}{dt} = \frac{\gamma}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (36),$$

where γ denotes the heat of formation of one gram-molecule from its ions.

From experimental determinations of the temperature

coefficient of dissociation of aqueous solutions, Arrhenius[1] has calculated the heats of formation of various molecules from their ions by means of this equation. It is important to observe that his results only apply to solutions in water.

Substance		γ at 21·5	γ at 35°
Acetic acid	CH_3COOH	+ 28	− 386
Propionic acid	C_2H_5COOH	− 183	− 557
Butyric acid	C_3H_7COOH	− 427	− 935
Phosphoric acid	H_3PO_4	− 2103	− 2458
Hydrofluoric acid	HF	− 3200	− 3549
Hydrochloric acid	HCl		− 1080
Nitric acid	HNO_3		− 1362
Soda	$NaOH$		− 1292
Potassium chloride	KCl		− 362
Barium chloride	$BaCl_2$		− 307
Sodium butyrate	C_3H_7COONa		+ 547

The numbers for strongly dissociated bodies are calculated from observations on decinormal solutions.

From this table, by adding to the heat of formation of water from its ions that caused by the completion of the dissociation of the acid, Arrhenius has calculated the total heats of neutralisation of soda by different acids.

Substance		Calculated	Observed
Hydrochloric acid	HCl	13447	13740
Hydrobromic „	HBr	13525	13750
Nitric „	HNO_3	13550	13680
Acetic „	CH_3COOH	13263	13400
Phosphoric „	H_3PO_4	14959	14830
Hydrofluoric „	HF	16320	16270

[1] *Zeits. für physikal. Chemie*, 1889, iv. p. 96; 1892, ix. p. 339.

Thus the divergences from the constant value are likewise explicable by this theory.

From equation (36) on page 191 it follows that, if the heat of formation is negative, that is, the heat of dissociation positive, the value of $d \log_e K/dt$ is also negative, and the dissociation must become less with increasing temperature. The conductivity is dependent on two factors, (1) the dissociation, and (2) the frictional resistance offered by the solution to the passage of an ion through it. If we call the reciprocal of this resistance the ionic fluidity of the solution, the molecular conductivity will be proportional to the dissociation and to the ionic fluidity. At infinite dilution the dissociation is complete, and the ions are so far apart that no change in temperature can affect the state of dissociation. Any alteration in conductivity with change of temperature must then be due to an alteration in fluidity, and, therefore, the temperature coefficient of fluidity can be determined by measuring the temperature coefficient of conductivity at a dilution so great that the molecular conductivity has reached its limiting value. Now the table on page 192 shews that the heats of formation from the ions have invariably a greater negative value at the higher temperature. From equation (36) it follows that the rate of decrease of dissociation with increase of temperature must therefore increase as the temperature rises. If the temperature coefficient of fluidity either decreases with rise of temperature, keeps constant, or increases more slowly than the negative coefficient of dissociation, it is clear that a maximum conductivity must be reached

at a certain temperature, beyond which any further heating will decrease the dissociation more than it increases the fluidity, and so, on the whole, diminish the conductivity.

Arrhenius calculated, from deductions from the equation, that solutions of the two slightly dissociated bodies, hypophosphoric and phosphoric acids, should have maximum values for the conductivity at 57° and 78° respectively. He then experimentally determined their conductivities at different temperatures, and actually found maxima at 55° and 75°. More recently Sack[1], by measuring the conductivity of copper sulphate solutions in closed vessels, found a maximum at 96° for a 0·64 per cent. solution. Calculation by Arrhenius' method gives 99° for a solution of this concentration.

These results must be considered, not only as a confirmation of the values found for the heat of formation of molecules from their ions, but also as evidence in favour of the general ideas of the dissociation theory.

76. Diffusion of Electrolytes in Solution. A theory of the diffusion of dissolved substances has been worked out by W. Nernst[2] and M. Planck[3] on the lines of the dissociation hypothesis. In our account of osmotic pressure we shewed how the laws of the diffusion of non-electrolytes could be deduced. We have now to

[1] *Wied. Ann.* 1891, XLIII. p. 212.

[2] *Zeits. für physikal. Chemie*, 1888, II. p. 613, or Nernst's "Theoretische Chemie."

[3] *Wied. Ann.* 1890, XL. p. 561.

extend the reasoning to cases in which free ions are present.

If the osmotic pressure-gradient were the only driving force, as in the first case, the different mobility of the two ions (e.g. H and Cl) would cause separation between them.

Thus suppose we had a solution of hydrochloric acid in the bottom of a tall glass cylinder, with pure water lying above it. The hydrogen ions travel faster than the chlorine, and carry their positive charges with them, leaving the lower layers negatively charged. Thus an electrostatic force is set up, which prevents the process of separation going far, and keeps the number of opposite ions in each part of the system very nearly the same. Nevertheless some separation does occur, and this explains the fact that water, in contact with an aqueous solution of an electrolyte, takes, with regard to it, a positive or negative potential as the positive or negative ion travels the faster.

The presence of a substance like ammonium chloride will reduce the restraining force of the electrostatic charges, and Arrhenius shewed that the addition of a large quantity of this salt increased the diffusion of hydrochloric acid, which is chiefly due to the hydrogen, in the ratio of 1 : 2·24.

In a layer of liquid in our cylinder, at a height x, let the concentration (i.e. number of gram-molecules per cubic centimetre) be c, and the osmotic pressure p. At a height $x + dx$ these become $c - dc$ and $p - dp$ respectively. The volume of the layer cut off by horizontal planes at these two heights is qdx, where q is the area of cross

section, and it contains $cqdx$ gram-molecules of electrolyte. The difference of pressure between the planes is dp, so that the force acting on the layer is qdp, and the force on one gram-molecule is $\frac{1}{c}\frac{dp}{dx}$. As we saw above (p. 139), Kohlrausch has calculated the mechanical force required to move different ions with unit velocity through dilute solutions. Let us call the velocities produced, when unit force acts on one gram-equivalent of the two ions, U and V respectively. The velocities, in our case, will be $\frac{U}{c}\frac{dp}{dx}$ and $\frac{V}{c}\frac{dp}{dx}$, so that the amounts passing across any cross section of the cylinder in a time dt are

$$-Uq\frac{dp}{dx}dt \text{ and } -Vq\frac{dp}{dx}dt.$$

If U is different from V, a difference of potential is set up, the effect of which, when a steady state is reached, is to make the ions travel together. If the potential gradient is dP/dx, the numbers of the two ions which would cross, under the action of this force alone, are

$$-Uqc\frac{dP}{dx}dt \text{ and } +Vqc\frac{dP}{dx}dt.$$

Under the action of both the osmotic and the electric forces the numbers of gram-equivalents which diffuse in a given time are equal, so that we get

$$dN = -Uq\,dt\left(\frac{dp}{dx}+c\frac{dP}{dx}\right) = -Vq\,dt\left(\frac{dp}{dx}-c\frac{dP}{dx}\right) \quad (37),$$

or eliminating dP/dx

$$dN = -\frac{2UV}{U+V}q\frac{dp}{dx}dt.$$

From the law of osmotic pressure

$$p = cRT,$$

since c is the reciprocal of the volume in which one gram-molecule is dissolved,

$$\therefore\ dN = -\frac{2UV}{U+V} RTq \frac{dc}{dx}\, dt.$$

Comparing this with the corresponding equation (7), p. 47, for non-electrolytes

$$dN = -Dq \frac{dc}{dx}\, dt,$$

we see that for electrolytes the diffusion constant is

$$D = \frac{2UV}{U+V} RT.$$

The following table gives a comparison between the observed and calculated values of D, the unit of time being the day.

Substance		D observed	D calculated
Hydrochloric acid	HCl	2·30	2·49
Nitric acid	HNO_3	2·22	2·27
Potash	KOH	1·85	2·10
Soda	$NaOH$	1·40	1.45
Sodium chloride	$NaCl$	1·11	1·12
,, nitrate	$NaNO_3$	1·03	1·06
,, formate	$NaCOOH$	0·95	0·95
,, acetate	$NaCH_3CO_2$	0·78	0·79
Ammonium chloride	NH_4Cl	1·33	1·44
Potassium nitrate	KNO_3	1·30	1·38

77. Contact Difference of Potential. We have already mentioned that the differences of potential

between liquids can be explained by the initial separation between the ions. Taking equation (37), which expresses the relation which must hold between the potential difference and the osmotic pressure in order that no cumulative separation of ions should go on, we get

$$\frac{dP}{dx} = \frac{1}{c}\frac{V-U}{V+U}\frac{dp}{dx},$$

or, since $p = cRT$,

$$\frac{dP}{dx} = \frac{RT}{p}\frac{V-U}{V+U}\frac{dp}{dx},$$

which gives on integration

$$P_2 - P_1 = RT\frac{V-U}{V+U}\log_e\frac{p_2}{p_1} \quad \ldots\ldots\ldots\ldots (38).$$

If we have absolutely pure water in contact with a solution, p_1 is zero, and the difference of potential apparently becomes infinite. But absolutely pure water cannot be obtained, and, as a matter of fact, great differences in the electromotive force are found for small differences in purity.

In a similar way the potential difference between the solutions of two different electrolytes or between solutions of the same electrolyte of different concentrations can be calculated. This is of great interest, for primary cells can be constructed with a plate of the same metal for both electrodes, by placing the electrodes in solutions of different substances, or even in solutions of the same substance at different concentrations. The theory described above can be applied to deduce the electromotive force of such cells by slightly modifying the equation.

The following table[1] gives a comparison between the observed and calculated values for the potential differences between solutions of different concentrations.

Electrolyte	C_1	C_2	E in volts (observed)	E in volts (calculated)
HCl	0·105	0·0180	0·0710	0·0717
,,	0·1	0·01	0·0926	0·0939
HBr	0·126	0·0132	0·0932	0·0917
KCl	0·125	0·0125	0·0532	0·0542
NaCl	0·125	0·0125	0·0402	0·0408
LiCl	0·1	0·01	0·0354	0·0336
NH_4Cl	0·1	0·01	0·0546	0·0531
NaBr	0·125	0·0125	0·0417	0·0404
$NaO_2C_2H_3$	0·125	0·0125	0·066	0·0604
NaOH	0·235	0·030	0·0178	0·0183
NH_4OH	0·305	0·032	0·024	0·0188
KOH	0·1	0·01	0·0348	0·0298

The dissociation theory thus gives a perfectly satisfactory explanation of the diffusion of electrolytes in solution, and of the differences in potential at the junctions of electrolytes.

The difference of potential between metals and electrolytes is explained in a similar manner. Nernst supposes that each metal in contact with an electrolyte has a definite solution pressure, analogous to the vapour pressure of a liquid, in consequence of which ions are detached from it, and go into solution, carrying their charges with them, and leaving the metal oppositely electrified. An

[1] W. Nernst. *Zeits. für physikal. Chemie*, 1889, IV. p. 161.

equation similar to (38) can be deduced for this case, and takes the form

$$e = RT \log_e \frac{P}{p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (39),$$

where p represents the osmotic pressure of the ions of the metal in the solution, and P the solution pressure of the metal of the electrode. The electromotive force of a voltaic cell will be given by

$$E = RT \left(\log_e \frac{P_1}{p_1} - \log_e \frac{P_2}{p_2} \right) \quad \ldots\ldots\ldots (40),$$

and thus depends on the differences between the solution pressures of the two electrodes. When a current passes, the ions of the metal with the smaller solution pressure are forced out of solution by the others, and deposited at the electrode.

The electromotive force of the cell

Ag | 0·1 normal $AgNO_3$ | 1·0 normal KCl with AgCl | Ag

in which silver electrodes are placed, one in silver nitrate, and the other in silver chloride and potassium chloride, was calculated by Nernst from this equation to be 0·52 volt, and observed by Ostwald to be 0·51 volt.

78. Dissociation of Water. Kohlrausch's experiments have shewn that the conductivity of pure water is exceedingly small, so that it can only be dissociated to a very slight extent. But this is only what we should expect, for the concentration is so great and the molecules are so crowded together that no dissociation can be permanent. Nevertheless, there are many indications that even chemically pure water would, if it could be pre-

pared, be slightly dissociated and possess some conducting power.

Methyl acetate and water react to form methyl alcohol and acetic acid at a rate proportional to the number of hydrogen ions or hydroxyl ions present in the solution. Wijs[1] used this reaction to measure the dissociation of water, by preparing an aqueous solution of methyl acetate carefully freed from acid or other impurity, and titrating it at intervals with standard alkali to measure the amount of acetic acid produced. The acid, as it is formed, accelerates this action, so that it is necessary to measure the rate of transformation just at the beginning. The concentration of the dissociated ions appeared to be about 10^{-6} gram equivalents per litre.

If two platinum or palladium electrodes, saturated with hydrogen, be placed, one in acid and the other in alkali, an electromotive force is set up between them, depending on the concentration of the hydrogen ions in the acid and of the hydroxyl ions in the alkali. From the laws of osmotic pressure Ostwald[2] has developed a theory of this relation, and from the observed electromotive forces has calculated that the concentration of the hydroxyl (and therefore also of the hydrogen) ions in pure water is $0{\cdot}9 \times 10^{-6}$.

Kohlrausch and Heydweiler[3] have distilled water in a vacuum and collected it in a glass vessel, which for ten years had been kept full of distilled water in order to dis-

[1] *Zeits. für physikal. Chemie*, 1893, 11, p. 492.
[2] *Ibid.*, 1893, 11, p. 521.
[3] *Wied. Ann.*, 1894, 53, p. 209.

solve out all the soluble constituents of the glass. By this means they obtained water so pure that its conductivity was $0{\cdot}014 \times 10^{-10}$ at 0°, and $0{\cdot}18 \times 10^{-10}$ at 18°. Now the temperature coefficient of conductivity depends on the influence of temperature on (1) the dissociation, and (2) the fluidity (p. 193). As the dilution increases and the dissociation becomes more complete, the effect of temperature on the dissociation gets less, and finally vanishes when the dilution is infinite, i.e. when the water is pure. The temperature coefficient then reaches a limit corresponding to its value for the fluidity alone. The conductivity, when this limit is reached, is, therefore, the conductivity of pure water. The limiting value can be estimated from a curve drawn to shew the variation of temperature coefficient with increasing dilution. The true conductivity of pure water was thus estimated as $0{\cdot}036 \times 10^{-10}$ at 18°. This gives for the concentration of the dissociated ions a value of 8×10^{-8} gram equivalents per litre.

We should expect the dissociation of the water to become greater as the amount of dissolved substance increased, and gave room for the ions to separate, and the fact that insoluble magnesium hydroxide is formed when a current is passed across the junction between strong and weak solutions of magnesium chloride, has been adduced as evidence that part of the current is carried by the water.

Attempts have, however, been made to explain this phenomenon by supposing that the hydrolytic dissociation

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$$

takes place as well as the electrolytic dissociation

$$MgCl_2 = \overset{+}{M}g'' + \overset{-}{C}l + \overset{-}{C}l,$$

but it is difficult to see, on this hypothesis, how it is that $Mg(OH)_2$ only appears at the junction.

It is interesting to observe that liquefied hydrochloric acid gas, like pure water, is a very bad conductor, while mixtures of the two conduct freely. Possibly no pure substance is an electrolyte, and mixture may be an essential condition for electrolytic conduction, though, if this is so, the conductivity of fused salts needs some further explanation.

79. Function of the Solvent. In the early development of the physical theory of solution no attention was paid to the part played by the solvent. It was looked on simply as furnishing a space into which the dissolving solid could diffuse, and, in the case of electrolytes, as providing a screen for separating the ions from one another. The very different power of various solvents, both in dissolving substances and in enabling them to conduct electricity when dissolved, directed attention to the general question of their influence, and measurements of conductivity of the same salt in water and alcohol were made by Fitzpatrick[1], Völlmer[2] and others.

The problem of the cause of solubility still remains unsolved. It is possible that it may depend on similarity in molecular motion on the part of solvent and substance dissolved, and this view is supported by the general rule that bodies are more soluble in liquids whose chemical con-

[1] *B.A. Report*, 1886, p. 328, and *Phil. Mag.*, 1887, 24, p. 378.

[2] *Wied. Ann.*, 1894, 52, p. 328.

stitution is similar to their own. Thus salts and mineral acids are usually soluble in water, while organic bodies will generally more readily dissolve in alcohol or benzene.

Towards the explanation of ionisation power some advance has been made. If the forces holding the ions together in a molecule are electrical in their nature (as is quite possible) it follows, as J. J. Thomson[1] has shewn, that they will be much weakened by immersing the molecule in a medium of high specific inductive capacity like water. The nature of this effect can be best explained by considering the influence of a mass of conducting material placed near two little particles charged with opposite kinds of electricity. The effect of the conductor can be represented by supposing that electrical images of opposite sign are formed just inside the conductor. The result is obviously to reduce the external effects of the charges and, therefore, their attraction for each other. The effect of an insulator of high specific inductive capacity is similar in kind, though rather less in magnitude. This may explain the differences observed in the molecular conductivities of the same salt dissolved in different solvents, such as water and alcohol for example, for other conditions being the same, the effect of solvents in loosening the connexion between two ions, i.e. their relative ionisation powers, will be proportional to their specific inductive capacities. Some figures which, as far as they go, confirm this idea for solutions of calcium

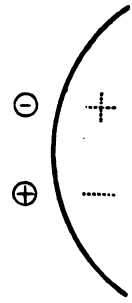


Fig. 20.

[1] *Phil. Mag.*, 1893, 36, p. 320.

chloride in water, methyl alcohol, and ethyl alcohol have been given by the present writer[1].

The specific inductive capacities of the three solvents are, according to Tereschin: water, 83·7: methyl alcohol, 32·65: ethyl alcohol, 25·8. If we suppose provisionally that the resistances offered by these solvents to the motion of the ions are in about the same ratios as their viscosities, we must divide these numbers by 100, 63 and 120, respectively. We then get for the theoretical ratio of the conductivities,

Water 100 Methyl Alcohol 63 Ethyl Alcohol 26.

An investigation by Völlmer shewed that, for many salts, the ratio of the conductivities in the three solvents was

Water 100 Methyl Alcohol 73 Ethyl Alcohol 34.

It seems probable, then, that the specific inductive capacity and the viscosity are important factors in determining the "relative ionisation power" of solvents.

It is worthy of remark that, as well as reducing the forces between ions, the conducting body in figure 20 will attract each ion to itself. The same thing would occur in a solvent of high specific inductive capacity. When the forces between two ions have been loosened, a slight collision with other molecules, or with molecules of the solvent, will suffice to cause dissociation, the liberated ions will be annexed by the solvent, and loose compounds will be formed. The ions, being readily passed on from one particle of the solvent to another, are able to work

[1] *Phil. Mag.*, 1894, 38, p. 392.

their way through the liquid under the action of the external electric forces.

If this theory represents the truth, we have three things, all of which may produce osmotic pressure effects. Firstly, the molecular and ionic impacts, secondly, chemical action between the unaltered molecules and the solvent, and, thirdly, combination between the ions and the solvent. In solutions of indifferent substances, and in very dilute solutions of most electrolytes, the first cause is probably the only one of importance, but in other cases all three may ultimately have to be considered. The fact that, according to the thermodynamical equation on p. 191, heat is in most cases developed when a molecule dissolved in water is resolved into its ions, again suggests that compounds between the ions and the solvent are formed. It is evident that such combination, provided the ions were free to move from particle to particle, would not prevent them from producing their proper osmotic pressure and electrical effects, and that they would behave, for all the other purposes of the theory, as free ions should.

80. Hydrate Theory of Solution. The question of chemical combination with the solvent has given rise to considerable discussion, and produced an independent theory of solution.

Before the laws of osmotic pressure and the allied phenomena were known, it was very generally held that solution was a case of chemical combination[1]. Chemical attraction of the solvent for the substance dissolved would

[1] See Tilden, *B.A. Report*, 1886, p. 444.

explain the *existence* of osmotic pressure, but gives no reason why it should have the particular value given by the same amount of substance in the gaseous state. In the case of dilute solutions of indifferent substances, it has, therefore, been very generally allowed that the chief cause of osmotic pressure is molecular impacts, but the influence of the solvent is recognised in equation (16) on page 69, and becomes sensible as the concentration increases. It was soon noticed, however, that bodies giving abnormal values for the osmotic pressure and acting as electrolytes, are just those for which the evidence of chemical action is strongest. This suggests the idea that chemical action is the condition necessary for ionisation, and that the formation of complex molecules, from which individual ions could be more easily removed by collision with other aggregates, is the meaning of conductivity.

Theories of solution based on these ideas have been recently framed by H. E. Armstrong[1], S. U. Pickering[2] and others. Pickering supposes that, when solvent is frozen out, some of the existing hydrate is decomposed, and the next lower one formed. From the heats of dilution of solutions of sulphuric acid of different strengths, he calculates the work required to do this, and, adding it to that required to compress the molecules dissolved, deduces the lowering of freezing-point[3]. The agreement of his numbers with observation shews that the excess of freezing-point depression can be calculated from the heat

[1] *Proc. R.S.*, 1886, No. 243.

[2] For general account see *Watts' Dict. Art. Solutions*, II.

[3] *B.A. Report*, 1890, p. 320.

of dilution, but does not decide whether that heat of dilution is due to the combination with additional molecules of water or (partly at any rate) to the resolution of some sulphuric acid molecules into their ions.

Pickering's main argument for the existence of hydrates in solution is based on the sudden changes in curvature, first noticed by Mendeléeff, which appear in the lines drawn to represent the variation of some physical property with the concentration. Pickering has made, for instance, a long and careful determination of the densities of sulphuric acid solutions of different strengths, and drawn a curve to shew his results. Changes of curvature appear at points corresponding to definite molecular proportions (e.g. $H_2SO_4 . H_2O$ and $H_2SO_4 4H_2O$). These changes can be more readily seen if a new curve is drawn between the concentration and the rate of change of density with concentration (i.e. the tangents at different points of the first curve). By this process of "differentiation" a series of straight lines is obtained with breaks at the positions where, in the first curve, changes of curvature appeared. Similar figures were drawn for the electric conductivity, expansion by heat, contraction on formation, heat of dissolution, heat capacity, refractive index, magnetic rotation and freezing-point, and changes of curvature were found at the same points for all. Ostwald however says[1] that the position of the breaks alters with change of temperature. With weak solutions it is impossible to say whether the points correspond to definite molecular proportions, owing to the smallness of the change in percentage

[1] *Watts' Dict. Art Solutions*, 1.

composition which would be caused by the addition of another water molecule to H_2SO_4, but the changes are of precisely the same character as in the case of stronger solutions, and are, apparently, due to the same cause. The thermal change, resulting from dilution of a strong solution, is of the same sign as that obtained by dissolving the solid in the first instance, and this also indicates that, if hydrates are present in concentrated, they are also present in dilute solutions. If we allow this, it follows that one acid molecule is able to combine with, or at all events to influence in some way, an enormous number of water molecules, and this is confirmed by other facts. For instance, the volume of substances in solution, as calculated by subtracting the volume of the water from the volume of the solution, is in general smaller than its volume in the solid state, and in some cases even comes out negative, shewing that the water has been compressed. This is shewn by the table on page 175. Even clearer evidence is furnished by the table of thermal capacities given on page 178. If we call the product of the specific heat and the molecular weight the molecular heat of the compound, it is sometimes found that the molecular heat of the solution is less than that of the water actually present. Thus the molecular heat of the solution $NaNO_3 + 25H_2O$ is 461·7, but, if $25H_2O$ more water be added, the molecular heat is not $461{\cdot}7 + (25 \times 18) = 911{\cdot}7$ but 904; again, if $50H_2O$ is added to this, the molecular heat is not $911{\cdot}7 + 900 = 1811{\cdot}7$ but 1791, and so on[1]. It is very improbable that the salt should so greatly reduce

[1] Tilden, *B.A. Report*, 1886, p. 455.

the heat capacity of a few molecules that the average capacity of the whole is lowered by as much as this, so that it seems necessary to suppose that the whole, or at all events a large part, of the added water is affected. It has also been argued that the diminution of vapour pressure is a proof that no water exists free from the influence of the salt, for, if it did, the evaporation, though it might proceed more slowly at first, would eventually reach the same amount as in the case of pure water.

Several hydrates, before unknown, were indicated by the presence of these breaks, and subsequently obtained in the solid form. Thus Pickering isolated $H_2SO_4 . 4H_2O$, $HBr . 3H_2O$, $HBr . 4H_2O$, $HCl . 3H_2O$, $HNO_3 . H_2O$ and $HNO_3 . 3H_2O$. He considers that the crystallization of a definite hydrate is strong evidence that it exists in solution, for bodies suddenly formed at the instant of precipitation come down as amorphous substances—a common observation in the processes of chemical analysis. Dilute sulphuric acid, dissolved in acetic acid, produces a smaller depression of the freezing point than the sum of those due to the acid and water separately, hence Pickering argues that no dissociation, but rather chemical union, resulting in a reduction in the number of molecules, has occurred.

Since the state of bodies in solution is similar to their state when gasified, a solid has to be not only liquefied but also vapourised when being dissolved. If allowance be made for the heat necessary to effect these changes, it is found that the process of solution, in every case, evolves heat, which indicates that chemical action has taken place.

Pickering supposes that the combination of large numbers of solvent molecules with one molecule of a body in solution is produced by a sort of induction of electric charges, just as a number of soft iron rods placed in a row can be made to cling together by bringing a magnet near the one at the end. Since the forces are equal in all directions, the mobility of the dissolved molecules is secured. Certain definite numbers of solvent molecules will be capable of more symmetrical arrangement than others, and will form hydrates, but their parts are freely interchangeable with each other. A dissolved molecule will be able to pass through a crevasse only when the number of solvent molecules requisite to keep it in solution can pass simultaneously, and this may explain the action of semipermeable membranes. Pickering[1] found that, when a mixture of alcohol and water was placed in a porous pot, and the whole immersed either in pure water or pure alcohol, the volume of liquid inside the porous pot increased, shewing that the phenomenon is due, not to the impermeability of the pot to either constituent alone, but to its impermeability to the solution as a whole.

81. Conclusion. We are now able, I think, by an extension of these ideas, to reconcile Pickering's observations with the dissociation theory. Since each particle of the salt extends its influence over a considerable region round it, the properties of the solution as a whole will depend on its percentage composition, and may quite probably undergo some change as the composition passes

[1] *Ber. Deut. Chem. Ges.*, 1891, 24, p. 3639.

through a value corresponding to simple molecular proportions. This will be independent of the arrangement of the parts of the salt molecule, since the influence of each part extends beyond its immediate neighbourhood, and dissociation into ions can still take place. We can, in fact, regard a considerable mass of the solution, containing, perhaps, several molecules and dissociated ions of salt, and hundreds of molecules of solvent, as chemically one large molecule, the parts of which are nevertheless to some extent physically independent of each other.

The phenomena of supersaturation and the conditions of equilibrium which hold between solids and solutions in contact with them (see pp. 18 to 25) indicate that it does not follow, because a certain hydrate or other compound is precipitated from a liquid on evaporation or cooling, that it therefore exists in the same state of molecular aggregation in the solution. But the adjustment of the chemical forces, which allows such a hydrate to be formed under proper conditions, makes it quite likely that, when the composition of the solution as a whole is the same as that of the hydrate, the fact should, by reason of the far-reaching influence of the chemical forces, become apparent in the physical properties. This at once explains how it happens that several of the hydrates, indicated by breaks in the solution diagrams, have actually been separated out as solids in the crystalline form. In fact, all the evidence which has been accumulated in favour of the existence of hydrates in solution, can be accounted for on this hypothesis, which at the same time allows us fully to accept the dissociation theory.

APPENDIX.

Freezing points. While this book was passing through the press, a paper by Nernst and Abegg[1] appeared, calling attention to the discrepancies which exist between the values obtained by different observers for the molecular depression of the freezing point. For instance, the following numbers have been obtained in the case of a one per cent. sugar solution in water: Raoult, 2·07; Arrhenius, 2·02; Pickering, 2·01; Jones, 2·18; Loomis, 1·81.

Nernst and Abegg point out that the observed stationary temperature may not always give the true freezing point, at which liquid and solid can exist together in equilibrium. A mass of a partly frozen liquid, uninfluenced by its surroundings, will tend to assume the temperature of the true freezing point. But a limited volume of liquid, radiating to an outer enclosure, tends to reach a "convergence" temperature, which depends on the amount of heat evolved by stirring and on the temperature of the enclosure; and, unless this convergence temperature coincides with the freezing point, or unless the rate of approach to the freezing point is very great compared

[1] *Zeits. für physikal. Chemie*, 1894, 15. 7, 681.

with the rate of approach to the convergence temperature, the thermometer will not shew the true freezing point.

The necessary corrections can be experimentally determined; and Nernst and Abegg obtained good agreement between the results of experiments performed under conditions so different, that the uncorrected numbers for the molecular depression of the freezing point of a one per cent. solution of sugar varied from 1·6 to 2·1. Their mean corrected value is about 1·86—a number which agrees exactly with that calculated from the melting point and heat of fusion of ice (p. 56).

TABLE OF ELECTRO-CHEMICAL PROPERTIES OF AQUEOUS SOLUTIONS,

COMPILED BY THE

REV. T. C. FITZPATRICK, M.A.,

FELLOW OF CHRIST'S COLLEGE, CAMBRIDGE,

and Reprinted, by permission, from the Report of the British Association for the Advancement of Science.

THE comparison of the numerical results of electrolytic observations is rendered difficult from the fact that the data are scattered in various periodicals and expressed by different observers in units that are not comparable without considerable labour. The following table has been compiled with the object of facilitating the comparison.

In the table are included all the observations, as far as they are known to the compiler, for the metallic salts and mineral acids; but amongst the solutions of organic substances are not given all those for which Ostwald has made observations, as it was thought that they would add unnecessarily to the size of the table. Observations for a number of additional substances will be found in Ostwald's papers in the *Journal für Chemie*, vols. xxxi., xxxii., and xxxiii., and in the *Zeitschrift für physikalische Chemie*, vol. i. With this restriction it is hoped that no important observations have been omitted, and that, in the reduction of results, expressed in such varied units, the table is sufficiently free from mistakes for it to be of service. The data included refer to the strength and specific gravity of solutions, with the corresponding conductivities, migration constants, and fluidities. The several columns are as follows:—

I. Percentage composition, *i.e.* the number of parts by weight of the salt (as represented by the chemical formula) in 100 parts of the solution.

II. The number of gramme molecules per litre, *i.e.* the number of grammes of the salt per litre divided by the chemical equivalent in grammes, as given for each salt.

III. The specific gravities of the solutions: in most cases the specific gravities of the solutions are not given by the observers, and the numbers given have been deduced from Gerlach's tables in the *Zeitschrift für analytische Chemie*, vol. viii. p. 243, &c.

IV. The temperatures at which the solutions have the specific gravities given in the previous column for the given strength of solution.

V. The conductivity, as expressed by the observer. In the cases in which the observer has expressed his results for specific molecular conductivity no numbers are given in this column.

VI. The temperature at which the conductivities of the solutions have been determined.

VII. The temperature coefficient referred to the conductivity at 18°, *i.e.* $\frac{1}{k_{18}}\left(\frac{\delta k_{18}}{\delta t}\right)$.

VIII. The specific molecular conductivity of the solutions at 18° in terms of the conductivity of mercury at 0°; the specific molecular conductivity is the conductivity of a column of the liquid 1 centimetre long and 1 square centimetre in section, divided by the number of gramme equivalents per litre.

In some few cases, in which no temperature coefficients have been determined, the results have been given for the temperature at which the observations were made.

The numbers given in the column are the values for the specific molecular conductivity $\times 10^9$.

IX. This column contains the values for specific molecular conductivity at 18° in C.G.S. units: they are obtained from those in the previous column by being multiplied by the value of the conductivity of mercury at 0° in C.G.S. units. This factor is $1{\cdot}063 \times 10^{-6}$.

X. The migration constant for the anion; for instance, in the case of copper sulphate ($CuSO_4$), for (SO_4).

XI. The temperatures at which the migration constants have been determined.

XII. The number of gramme molecules per litre, as defined for column II., for which the fluidity data are given in the following columns.

XIII. The fluidity of the solutions of the strength given in the previous column.

Most of the results given for the fluidity of solutions are expressed in terms of the fluidity of water at the same temperature: to obtain the absolute values for the solutions they have been multiplied by the value for the fluidity of water at the given temperature. The values used for this purpose have been taken from Sprung's observations for the viscosity of water given in *Poggendorff's Annalen*, vol. clix. p. 1.

To obtain the values for fluidity in C.G.S. units, the numbers in this column must be multiplied by the factor ·1019.

XIV. The temperature at which the solutions have the fluidity given in the previous column.

XV. The temperature coefficient of fluidity at 18°, that is, $\frac{1}{f_{18}}\left(\frac{\delta f_{18}}{\delta t}\right)$.

XVI. In the last column are given the references to the various papers from which the data are taken: against each reference will be found a number, which appears also against the first of the data which have been taken from the paper in question.

| | | |

·907	·25	1·0045	15·5	80·9	25	—	—	3268	—	—	—	—	—	—	[5] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
1·807	·5	1·0086	15·5	77·9	25	—	—	3166	—	—	—	—	—	—	
·0286	·00784	—	—	2·66[5]	18	—	3395	3609	—	—	—	—	—	—	
·057	·0157	—	—	5·28	18	—	3369	3581	—	—	—	—	—	—	
·114	·0314	—	—	10·4	18	—	3323	3532	—	—	—	—	—	—	
·228	·0627	—	—	20·6	18	—	3289	3496	—	—	—	—	—	—	
·456	·1255	1·0018	15·5	40·5	18	—	3234	3438	—	—	—	—	—	—	
·910	·251	1·0046	15·5	78·7	18	—	3138	3336	—	—	—	—	—	—	
1·813	·502	1·0090	15·5	151·3	18	—	3014	3204	—	—	—	—	—	—	

Potassium Chloride.

Equivalent Gramme Molecule, KCl, 74·59.

·0000746	·00001	—	—	—	18	—	1216[1]	1293	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000149	·00002	—	—	—	18	—	1217	1294	—	—	—	—	—	—	
·000448	·00006	—	—	—	18	—	1212	1288	—	—	—	—	—	—	
·000746	·0001	—	—	—	18	—	1209	1285	—	—	—	—	—	—	
·00149	·0002	—	—	—	18	—	1209	1285	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
·00448	·0006	—	—	—	18	—	1199	1275	—	—	—	—	—	—	
·00746	·001	—	—	—	18	—	1193	1268	—	—	—	—	—	—	
·0149	·002	—	—	—	18	—	1185	1260	—	—	·125	992[3]	20	—	
·0448	·006	—	—	—	18	—	1162	1235	—	—	·25	995	20	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
·0746	·01	—	—	—	18	·0221	1147	1219	—	—	·5	997	20	—	
·224	·03	—	—	—	18	—	1107	1178	·503[2]	—	1·0	997	20	—	
·372	·05	1·0019	15	—	18	—	1083	1151	—	—	1·466	987[4]	20	·0219	
·743	·1	1·0046	15	—	18	—	1047	1113	—	—	3·432	956	20	·0191	[4] Sprung, *Pogg. Annal.* vol. clix. p. 1.
3·64	·5	1·0228	15	—	18	·0206	958	1018	—	—	—	—	—	—	
5·15	·714	1·0342	7·2	—	—	—	—	—	·515	—	·0625	986[5]	20	—	
7·13	1·0	1·0457	18	—	18	·0199	919	977	—	—	·125	986	20	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
13·1	1·94	1·1034	4·5	—	—	—	—	—	·516	—	·25	987	20	—	
17·1	2·55	1·1155	12·4	—	—	—	—	—	·516	—	·5	988	20	—	
19·7	3·0	1·1359	15	—	18	·0170	827	879	—	—	1·0	990	20	—	[6] Bouty, *Journal de Physique*, vol. vi. p. 10.
·00746	·001	—	—	1·29[6]	18	—	—	1250	—	—	1·0	997[7]	20	—	
·0746	·01	—	—	12·1	18	—	—	1206	—	—	—	—	—	—	[7] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·743	·1	1·0046	15	113·0	18	—	—	1130	—	—	—	—	—	—	
1·48	·2	1·0096	15	220·0	18	—	—	1100	—	—	—	—	—	—	
3·74	·5	1·0228	15	508·0	18	—	—	1016	—	—	—	—	—	—	
7·13	1·0	1·0457	15	991·0	18	—	—	991	—	—	—	—	—	—	
13·7	2·0	1·0912	15	1888·0	18	—	—	944	—	—	—	—	—	—	
9·7	3·0	1·1359	15	2742·0	18	—	—	914	—	—	—	—	—	—	

| | | |

·907	·25	1·0045	15·5	80·9	25	—	—	3268	—	—	—	—	—	—	[5] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
1·807	·5	1·0086	15·5	77·9	25	—	—	3166	—	—	—	—	—	—	
·0286	·00784	—	—	2·66[5]	18	—	3395	3609	—	—	—	—	—	—	
·057	·0157	—	—	5·28	18	—	3369	3581	—	—	—	—	—	—	
·114	·0314	—	—	10·4	18	—	3323	3532	—	—	—	—	—	—	
·228	·0627	—	—	20·6	18	—	3289	3496	—	—	—	—	—	—	
·456	·1255	1·0018	15·5	40·5	18	—	3234	3438	—	—	—	—	—	—	
·910	·251	1·0046	15·5	78·7	18	—	3138	3336	—	—	—	—	—	—	
1·813	·502	1·0090	15·5	151·3	18	—	3014	3204	—	—	—	—	—	—	

Potassium Chloride.

Equivalent Gramme Molecule, KCl, 74·59.

·0000746	·00001	—	—	—	18	—	1216[1]	1293	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000149	·00002	—	—	—	18	—	1217	1294	—	—	—	—	—	—	
·000448	·00006	—	—	—	18	—	1212	1288	—	—	—	—	—	—	
·000746	·0001	—	—	—	18	—	1209	1285	—	—	—	—	—	—	
·00149	·0002	—	—	—	18	—	1209	1285	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
·00448	·0006	—	—	—	18	—	1199	1275	—	—	—	—	—	—	
·00746	·001	—	—	—	18	—	1193	1268	—	—	—	—	—	—	
·0149	·002	—	—	—	18	—	1185	1260	—	—	·125	992[3]	20	—	
·0448	·006	—	—	—	18	—	1162	1235	—	—	·25	995	20	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
·0746	·01	—	—	—	18	·0221	1147	1219	—	—	·5	997	20	—	
·224	·03	—	—	—	18	—	1107	1178	·503[2]	—	1·0	997	20	—	
·372	·05	1·0019	15	—	18	—	1083	1151	—	—	1·466	987[4]	20	·0219	
·743	·1	1·0046	15	—	18	—	1047	1113	—	—	3·432	956	20	·0191	[4] Sprung, *Pogg. Annal.* vol. clix. p. 1.
3·64	·5	1·0228	15	—	18	·0206	958	1018	—	—	—	—	—	—	
5·15	·714	1·0342	7·2	—	—	—	—	—	·515	—	·0625	986[5]	20	—	
7·13	1·0	1·0457	18	—	18	·0199	919	977	—	—	·125	986	20	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
13·1	1·94	1·1034	4·5	—	—	—	—	—	·516	—	·25	987	20	—	
17·1	2·55	1·1155	12·4	—	—	—	—	—	·516	—	·5	988	20	—	
19·7	3·0	1·1359	15	—	18	·0170	827	879	—	—	1·0	990	20	—	[6] Bouty, *Journal de Physique*, vol. vi. p. 10.
·00746	·001	—	—	1·29[6]	18	—	—	1250	—	—	1·0	997[7]	20	—	
·0746	·01	—	—	12·1	18	—	—	1206	—	—	—	—	—	—	
·743	·1	1·0046	15	113·0	18	—	—	1130	—	—	—	—	—	—	[7] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
1·48	·2	1·0096	15	220·0	18	—	—	1100	—	—	—	—	—	—	
3·74	·5	1·0228	15	508·0	18	—	—	1016	—	—	—	—	—	—	
7·13	1·0	1·0457	15	991·0	18	—	—	991	—	—	—	—	—	—	
13·7	2·0	1·0912	15	1888·0	18	—	—	944	—	—	—	—	—	—	
9·7	3·0	1·1359	15	2742·0	18	—	—	914	—	—	—	—	—	—	

Potassium Chloride—*continued.*

Equivalent Gramme Molecule, KCl, 74·59.

			°		°					°				°		
·00725	·000976	—	—	142·3[8]	25	·0221	—	1310	—	—	—	—	—	—	—	[8] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0145	·00195	—	—	138·6	25	—	—	1276	—	—	—	—	—	—	—	
·029	·0039	—	—	134·8	25	—	—	1241	—	—	—	—	—	—	—	[9] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·058	·0078	—	—	131·1	25	—	—	1207	—	—	—	—	—	—	—	
·116	·0156	—	—	127·6	25	—	—	1174	—	—	—	—	—	—	—	
·232	·0312	1·0008	15	124·2	25	—	—	1143	—	—	—	—	—	—	—	
·0072	·00097	—	—	—	18	·0236	1180[9]	1254	—	—	—	—	—	—	—	
·0142	·0019	—	—	—	18	·0231	1140	1211	—	—	—	—	—	—	—	
·0283	·0038	—	—	—	18	·0222	1110	1180	—	—	—	—	—	—	—	
·0746	·0100	—	—	—	18	·0220	1080	1148	—	—	—	—	—	—	—	
·137	·0184	—	—	—	18	·0218	1060	1127	—	—	—	—	—	—	—	

Ammonium Chloride.

Equivalent Gramme Molecule, NH_4Cl, 53·5.

·0000535	·00001	—	—	—	18	—	1205[1]	1281	—	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000107	·00002	—	—	—	18	—	1209	1285	—	—	—	—	—	—	—	
·000321	·00006	—	—	—	18	—	1215	1292	—	—	—	—	—	—	—	
·000535	·0001	—	—	—	18	—	1209	1285	—	—	—	—	—	—	—	[2] Sprung, *Pogg. Annal.* vol. clix. p. 1.
·00107	·0002	—	—	—	18	—	1204	1280	—	—	—	—	—	—	—	
·00321	·0006	—	—	—	18	—	1197	1273	—	—	—	—	—	—	—	
·00535	·001	—	—	—	18	—	1190	1265	—	—	·693	989[2]	20	—	—	[3] Grotian, *Pogg. Annal.* vol. clx. p. 262.
·0107	·002	—	—	—	18	—	1180	1255	—	—	1·625	1009	20	—	—	
·0321	·006	—	—	—	18	—	1157	1230	—	—	3·069	1005	20	—	—	
·0535	·01	—	—	—	18	·0226	1142	1214	—	—	4·666	980	20	—	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·1605	·03	—	—	—	18	—	1101	1171	—	—	—	—	—	—	—	
·267	·05	1·0002	15·0	—	18	—	1078	1146	—	—	·95	996[3]	20	·0229	—	
·534	·1	1·0013	15·0	—	18	—	1035	1100	—	—	1·925	985	20	·0212	—	
·57	·107	1·0019	7·0	—	—	—	—	—	·508[3]	—	2·93	1011	20	·0198	—	
2·65	·5	1·0084	15·0	—	18	·0204	948	1007	—	—	3·956	987	20	·019	—	[5] Hittorf, *Pogg. Annal.* vol. xcviii. p. 33.
3·44	·65	1·0113	9·8	—	—	—	—	—	·514	—	—	—	—	—	—	
5·263	1·0	1·0165	15·0	—	18	·0198	907	964	—	—	1·0	998[4]	20	—	—	
7·59	1·45	1·0241	9·8	—	—	—	—	—	·514	—	—	—	—	—	—	
—	3·0	1·0461	15·0	—	18	·0172	825	877	—	—	—	—	—	—	—	
15·92	3·12	1·0483	11·8	—	—	—	—	—	·517	—	—	—	—	—	—	
—	5·0	1·0730	15·0	—	18	·0155	752	799	—	—	—	—	—	—	—	

·334	·0625	1·0005	15·0	65·9[6]	18	—	1054	1120	—	—	—	—	—	—	[6] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi. No. 3.
·667	·125	1·0018	15·0	127·5	18	—	1020	1084	—	—	—	—	—	—	
1·331	·25	1·0042	15·0	244·0	18	—	976	1037	—	—	—	—	—	—	
2·65	·5	1·0084	15·0	466·0	18	—	932	991	—	—	—	—	—	—	
·0081	·00152	—	—	—	18	·0233	1200[7]	1276	—	—	—	—	—	—	[7] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0151	·00282	—	—	—	18	·0226	1150	1222	—	—	—	—	—	—	
·0309	·00578	—	—	—	18	·0224	1120	1190	—	—	—	—	—	—	
·053	·0099	—	—	—	18	·0224	1090	1159	—	—	—	—	—	—	
·0942	·0176	—	—	—	18	·0221	1060	1127	—	—	—	—	—	—	
·183	·0342	—	—	—	18	·0221	1030	1095	—	—	—	—	—	—	

Sodium Chloride.

Equivalent Gramme Molecule, NaCl, 58·5.

·000058	·00001	—	—	—	18	—	1024[1]	1088	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000117	·00002	—	—	—	18	—	1028	1093	—	—	—	—	—	—	
·000351	·00006	—	—	—	18	—	1027	1092	—	—	—	—	—	—	
·000585	·0001	—	—	—	18	—	1029	1094	—	—	—	—	—	—	
·00117	·0002	—	—	—	18	—	1018	1082	—	—	1·437	854[2]	20	·0245	[2] Sprung, *Pogg. Annal.* vol. clix. p. 13.
·00351	·0006	—	—	—	18	—	1014	1077	—	—	2·704	740	20	·0243	
·00585	·001	—	—	—	18	—	1008	1071	—	—	5·013	558	20	·0252	
·0117	·002	—	—	—	18	—	998	1061	—	—	—	—	—	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0351	·006	—	—	—	18	—	976	1037	—	—	—	—	—	—	
·0585	·01	—	—	—	18	·0238	962	1023	—	—	1·0	896[3]	20	—	
·1755	·03	1·0006	15·0	—	18	—	920	978	—	—	—	—	—	—	
·292	·05	1·0015	15·0	—	18	—	897	953	—	—	—	—	—	—	
·31	·055	1·0023	5·6	—	—	—	—	—	·622[5]	—	·0625	980[4]	20	—	[4] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
·583	·1	1·0038	15·0	—	18	—	865	919	—	—	·125	975	20	—	
·945	·162	1·0068	17·4	—	—	—	—	—	·628	—	·25	963	20	—	
2·865	·5	1·0207	15·0	—	18	·0220	757	804	—	—	·5	942	20	—	[5] Hittorf, *Pogg. Annal.* vol. cvi. p. 374.
4·61	·814	1·0334	16·2	—	—	—	—	—	·634	—	1·0	890	20	—	
5·62	1·0	1·0406	15·0	—	18	·0218	695	739	—	—	—	—	—	—	[6] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
15·03	2·867	1·1159	8·6	—	—	—	—	—	·647	—	—	—	—	—	
15·71	3·0	1·1171	15·0	—	18	·0213	528	561	—	—	—	—	—	—	
22·34	4·477	1·1716	13·0	—	—	—	—	—	·648	—	—	—	—	—	
24·6	5·0	1·1890	15·0	—	18	·0227	398	423	—	—	—	—	—	—	
·365	·0625	1·0021	15·0	54·2[6]	18	—	867	921	—	—	—	—	—	—	
·728	·125	1·0050	15·0	104·2	18	—	834	886	—	—	—	—	—	—	

Sodium Chloride—*continued.*

Equivalent Gramme Molecule, NaCl, 58·5.

			°		°					°				°		
1·44	·25	1·0105	15·0	197·6	18	—	790	840	—	—	—	—	—	—	[7] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 80.
2·86	·5	1·0207	15·0	369·0	18	—	738	784	—	—	—	—	—	—	
·0058	·000976	—	—	119·5[7]	25	—	—	1089	—	—	—	—	—	—	
·0115	·00195	—	—	116·3	25	—	—	1060	—	—	—	—	—	—	[8] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·023	·0039	—	—	112·1	25	—	—	1021	—	—	—	—	—	—	
·046	·0078	—	—	110·1	25	—	—	1003	—	—	—	—	—	—	
·092	·0156	—	—	107·0	25	—	—	975	—	—	—	—	—	—	
·183	·0312	1·0006	15·0	104·0	25	—	—	948	—	—	—	—	—	—	
·00643	·0011	—	—	—	18	·0236	970[8]	1031	—	—	—	—	—	—	
·00936	·0016	—	—	—	18	·0232	950	1010	—	—	—	—	—	—	
·0287	·0049	—	—	—	18	·0232	920	978	—	—	—	—	—	—	

Lithium Chloride.

Equivalent Gramme Molecule, LiCl, 42·5.

·0000425	·00001	—	—	—	18	—	965[1]	1026	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000085	·00002	—	—	—	18	—	955	1015	—	—	—	—	—	—	
·000255	·00006	—	—	—	18	—	945	1004	—	—	—	—	—	—	
·000425	·0001	—	—	—	18	—	943	1002	—	—	—	—	—	—	
·00085	·0002	—	—	—	18	—	938	997	—	—	—	—	—	—	
·00255	·0006	—	—	—	18	—	926	984	—	—	1·908	741[2]	20	·0252	[2] Sprung, *Pogg. Annal.* vol. clix. p. 17.
·00425	·001	—	—	—	18	—	921	979	—	—	3·54	584	20	·0248	
·0085	·002	—	—	—	18	—	911	968	—	—	7·305	313	20	·0247	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 88.
·0255	·006	—	—	—	18	—	889	945	—	—	—	—	—	—	
·0425	·01	—	—	—	18	·0232	875	930	—	—	—	—	—	—	
·1275	·03	—	—	—	18	—	834	887	—	—	·125	957[3]	20	—	
—	·042	—	—	—	—	—	—	—	·674[6]	—	·25	937	20	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·212	·05	1·0006	15	—	18	—	811	862	—	—	·5	907	20	—	
·424	·1	1·0021	15	—	18	—	775	824	—	—	1·0	863	20	—	
—	·11	—	—	—	—	—	—	—	·699	—	—	—	—	—	
—	·235	—	—	—	—	—	—	—	·718	—	—	—	—	—	
2·985	·5	1·0126	15	—	18	·0229	661	703	—	—	1·0	857[4]	20	—	[5] Kuschel, *Wied. Annal*, vol. xiii. p. 295.
—	·809	—	—	—	—	—	—	—	·739	—	—	—	—	—	
4·146	1·0	1·0249	15	—	18	·0225	591	628	—	—	—	—	—	—	
7·757	1·784	—	—	—	—	—	—	—	·738	—	—	—	—	—	

12·0	3·0	1·0700	15	—	18	·0218	421	447	—	—	—	—	—	—	[6] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
13·91	3·213	—	—	—	—	—	—	—	·753	—	—	—	—	—	
19·12	5·0	1·1110	15	—	18	·0220	303	322	—	—	—	—	—	—	
26·93	6·895	—	—	—	—	—	—	—	·773	—	—	—	—	—	
34·91	10·0	1·2173	15	—	18	·0251	106	113	—	—	—	—	—	—	
·0083	·00195	—	—	—	18	—	897[6]	954	—	—	—	—	—	—	
·0165	·0039	—	—	—	18	·0234	882	938	—	—	—	—	—	—	
·0331	·0078	—	—	—	18	—	874	929	—	—	—	—	—	—	
·0662	·0156	—	—	—	18	—	849	902	—	—	—	—	—	—	
·1325	·0312	—	—	—	18	—	820	871	—	—	—	—	—	—	
·265	·0625	—	—	—	18	—	784	833	—	—	—	—	—	—	
·53	·125	1·0028	15	—	18	—	745	792	—	—	—	—	—	—	
1·056	·25	1·0063	15	—	18	—	694	738	—	—	—	—	—	—	

Strontium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}SrCl_2$, 79·02.

·00506	·00064	—	—	—	18	·0244	1070[1]	1137	—	—	·969	867[2]	20	·0244	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0069	·00087	—	—	—	18	—	1040	1105	—	—	1·41	772	20	·0235	
·0111	·0014	—	—	—	18	·0240	1000	1063	—	—	3·31	611	20	—	
·0229	·0029	—	—	—	18	·0237	880	935	—	—	5·508	400	20	—	[2] Sprung, *Pogg. Annal.* vol. clix. p. 18.
—	·5	—	—	353[5]	18	·0217	706	—	—	—	·125	954[3]	20	—	[3] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
—	1·0	—	—	640	18	·0212	640	—	—	—	·25	923	20	—	
—	1·5	—	—	882	18	·0208	588	—	—	—	·5	860	20	—	
—	2·0	—	—	1082	18	·0204	541	—	—	—	1·0	752	20	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
—	2·5	—	—	1250	18	—	500	—	—	—	—	—	—	—	
—	3·0	—	—	1387	18	—	462	—	—	—	·125	960[4]	20	—	[5] Kohlrausch, *Wied. Annal.* vol. vi. p. 148.
—	3·5	—	—	1499	18	—	426	—	—	—	·25	941	20	—	
—	—	—	—	—	—	—	—	—	—	—	·5	911	20	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	853	20	—	

Barium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}BaCl_2$, 104.

·000104	·00001	—	—	—	18	—	1142[1]	1214	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000208	·00002	—	—	—	18	—	1144	1216	—	—	·783	898[2]	20	·0240	
·000624	·00006	—	—	—	18	—	1133	1204	—	—	1·715	807	20	·0226	
·00104	·0001	—	—	—	18	—	1126	1197	—	—	2·955	683	20	·0222	[2] Sprung, *Pogg. Annal.* vol. clix. p. 18.
·00208	·0002	—	—	—	18	—	1118	1189	—	—	—	—	—	—	

Barium Chloride—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}BaCl_2$, 104.

			°		°					°			°		
·00624	·0006	—	—	—	18	—	1102	1172	—	—	1·0	883[3]	20	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0104	·001	—	—	—	18	—	1092	1161	—	—	—	—	—	—	
·0208	·002	—	—	—	18	—	1074	1142	—	—	·125	963[4]	20	—	
·0624	·006	—	—	—	18	—	1031	1096	—	—	·25	951	20	—	
·104	·01	1·0001	15·0	—	18	·0234	1006	1069	—	—	·5	923	20	—	
·311	·03	1·0022	15·0	—	18	—	939	998	—	—	1·0	868	20	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 35.
·518	·05	1·0044	15·0	—	18	—	904	961	—	—	—	—	—	—	
·784	·076	1·0070	9·6	—	—	—	—	—	·61[6]	—	·0625	970[5]	20	—	
1·03	·1	1·0094	15·0	—	18	—	861	915	—	—	·125	955	20	—	
1·24	·12	1·0112	19·7	—	—	—	—	—	·616	—	·25	926	20	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
4·97	·5	1·0457	15·0	—	18	·0214	725	771	—	—	·5	867	20	—	
9·54	1·0	1·0905	15·0	—	18	·0207	658	699	—	—	1·0	760	20	—	
10·65	1·13	1·1028	19·0	—	—	—	—	—	·642	—	—	—	—	—	[6] Hittorf, *Pogg. Annal.* vol. cvi. p. 379.
21·6	2·55	1·2277	14·4	—	—	—	—	—	·663	—	—	—	—	—	
23·5	2·88	1·2546	7·3	—	—	—	—	—	·664	—	—	—	—	—	
—	3·0	1·2655	15·0	—	18	·0193	487	518	—	—	—	—	—	—	

Calcium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CaCl_2$, 55·46.

·434	·078	1·0036	20·0	—	—	—	—	—	·683[2]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 148.
·718	·13	1·0062	9·0	—	—	—	—	—	·673	—	—	—	—	—	
2·71	·5	1·0231	15·0	348·0	18	·0218	696[1]	740	—	—	—	—	—	—	
4·56	·853	1·0382	20·0	—	—	—	—	—	·683	—	3·098	630[2]	20	·0232	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.
5·307	1·0	1·0451	15·0	633·0	18	·0213	633	673	—	—	7·437	251	20	·0235	
10·19	2·0	1·0887	15·0	1083·0	18	·0207	542	576	—	—	9·984	111·4	20	·0309	
14·71	3·0	1·1309	15·0	1389·0	18	·0203	463	492	—	—	—	—	—	—	
18·93	4·0	1·1718	15·0	1583·0	18	·0201	398	423	—	—	·125	959[4]	20	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 19.
20·2	4·3	1·1819	20·8	—	—	—	—	—	·727	—	·25	942	20	—	
22·88	5·0	1·2119	15·0	1666·0	18	·0202	333	354	—	—	·5	906	20	—	
26·6	6·0	1·2510	15·0	1644·0	18	·0206	274	291	—	—	1·0	844	20	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
26·73	6·04	1·2529	9·7	—	—	—	—	—	·749	—	—	—	—	—	
29·75	6·91	1·2884	2·8	—	—	—	—	—	·765	—	·125	952[5]	20	—	
30·11	7·0	1·2892	15·0	1541·0	18	·0216	220	234	—	—	·25	922	20	—	
32·6	7·73	1·3160	12·4	—	—	—	—	—	·771	—	·5	858	20	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
33·37	8·0	1·3267	15·0	1370·0	18	·0231	171	182	—	—	1·0	751	20	—	
36·6	9·0	1·3633	15·0	1177·0	18	·0244	130	138	—	—	—	—	—	—	
37·08	9·14	1·3637	20·0	—	—	—	—	—	·78	—	—	—	—	—	

·00549	·00099	—	—	—	18	—	990[6]	1052	—	—	—	—	—	—	[6] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0089	·0016	—	—	—	18	—	970	1031	—	—	—	—	—	—	
·015	·0027	—	—	—	18	—	930	989	—	—	—	—	—	—	
·017	·00312	—	—	32·67	18	—	1043	1109	—	—	—	—	—	—	[7] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxvi. p. 377.
·034	·00625	—	—	63·0	18	—	1008	1071	—	—	—	—	—	—	
·069	·0125	—	—	120·2	18	—	972	1033	—	—	—	—	—	—	
·138	·025	—	—	228·0	18	—	912	969	—	—	—	—	—	—	
·277	·05	1·0017	15·0	430·5	18	—	861	915	—	—	—	—	—	—	
·552	·1	1·0043	15·0	809·0	18	—	809	860	—	—	—	—	—	—	
1·1	·2	1·0093	15·0	1442·0	18	—	721	766	—	—	—	—	—	—	

Magnesium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}MgCl_2$, 47·46.

·0046	·000975	—	—	119·9[1]	25	—	—	1070	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 109.
·0092	·00195	—	—	115·8	25	—	—	1043	—	—	—	—	—	—	
·0185	·0039	—	—	111·6	25	—	—	1010	—	—	·125	1071[5]	25	—	
·037	·00781	—	—	107·2	25	—	—	972	—	—	·25	1046	25	—	
·074	·0156	—	—	102·4	25	—	—	930	—	—	·5	999	25	—	[2] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 194.
·148	·0312	1·0005	15·0	97·3	25	—	—	885	—	—	1·0	957	25	—	
·0475	·01	—	—	—	18	·0241	950[2]	1010	—	—	—	—	—	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·142	·03	1·0004	15·0	—	18	—	878	932	—	—	·125	950[6]	20	—	
·237	·05	1·0013	15·0	—	18	—	841	894	—	—	·25	915	20	—	
·412	·087	1·0035	6·0	—	—	—	—	—	·678[4]	—	·5	848	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 383.
·473	·1	1·0035	15·0	—	18	—	794	844	—	—	1·0	741	20	—	
·773	·164	1·0065	15·0	—	—	—	—	—	·677	—	—	—	—	—	
2·327	·5	1·0197	15·0	—	18	·0226	665	706	—	—	—	—	—	—	[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
4·31	·941	1·0366	14·4	—	—	—	—	—	·706	—	—	—	—	—	
4·57	1·0	1·0386	15·0	—	18	·0223	593	631	—	—	—	—	—	—	
12·81	3·0	1·1114	15·0	—	18	·0224	400	425	—	—	—	—	—	—	
20·12	5·0	1·1792	15·0	—	18	·0238	262	288	—	—	—	—	—	—	
21·53	5·41	1·1934	15·0	—	—	—	—	—	·779	—	—	—	—	—	
28·71	7·67	1·2685	5·6	—	—	—	—	—	·866	—	—	—	—	—	[6] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
—	10·0	—	—	—	18	·0340	62	66	—	—	—	—	—	—	
·0073	·00154	—	—	—	—	—	920[3]	978	—	—	—	—	—	—	
·0091	·00192	—	—	—	—	—	910	967	—	—	—	—	—	—	
·0153	·00322	—	—	—	—	—	900	975	—	—	—	—	—	—	

Zinc Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}ZnCl_2$, 67·82.

			°		°					°				°	
·000068	·00001	—	—	—	—	—	1036[1]	1101	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000136	·00002	—	—	—	—	—	1035	1100	—	—	—	—	—	—	
·000407	·00006	—	—	—	—	—	1031	1096	—	—	—	—	—	—	
·000678	·0001	—	—	—	—	—	1029	1094	—	—	—	—	—	—	
·001356	·0002	—	—	—	—	—	1020	1084	—	—	—	—	—	—	
·00407	·0006	—	—	—	—	—	1004	1067	—	—	—	—	—	—	
·00678	·001	—	—	—	—	—	994	1057	—	—	1·0	777[4]	17·6	—	[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·01356	·002	—	—	—	—	—	979	1040	—	—	—	—	—	—	
·0407	·006	—	—	—	—	—	939	998	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 397.
·0678	·01	—	—	—	—	·0239	915	973	—	—	—	—	—	—	
·2034	·03	1·0007	19·5	—	—	—	851	905	—	—	·125	1067[5]	25·0	—	
·3	—	—	—	—	—	—	—	—	·7[3]	—	·25	1038	25·0	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·337	·05	1·0023	19·5	—	—	—	817	868	—	—	·5	997	25·0	—	
·672	·1	1·0062	19·5	—	—	—	768	816	—	—	1·0	919	25·0	—	
3·28	·5	1·0312	19·5	—	—	—	601	639	—	—	—	—	—	—	
6·4	1·0	1·0570	19·5	—	—	—	514	546	—	—	—	—	—	—	
17·5	3·0	1·1600	19·5	—	—	—	280	298	—	—	—	—	—	—	[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
26·52	—	—	—	—	—	—	—	—	1·08	—	—	—	—	—	
26·88	5·0	1·2587	19·5	—	—	—	180	191	—	—	—	—	—	—	
45·35	10·0	1·4921	19·5	—	—	—	60	64	—	—	—	—	—	—	
															[6] Long, *Wied. Annal.* vol. xi. p. 37.
·0117	·00173	—	—	—	—	—	910[2]	967	—	—	—	—	—	—	
·023	·0034	—	—	—	—	—	870	924	—	—	—	—	—	—	
2·5	·378	1·024	15·0	258[6]	18	·0213	682	725	—	—	—	—	—	—	
5·0	·774	1·048	15·0	452	18	·0192	584	621	—	—	—	—	—	—	
10·0	1·617	1·094	15·0	680	18	·0165	421	447	—	—	—	—	—	—	
20·0	3·517	1·190	15·0	853	18	·0156	243	258	—	—	—	—	—	—	
30·0	5·76	1·299	15·0	866	18	·0172	150	160	—	—	—	—	—	—	
40·0	8·41	1·423	15·0	790	18	·0198	94	100	—	—	—	—	—	—	
50·0	11·6	1·570	15·0	589	18	·0232	51	54	—	—	—	—	—	—	
60·0	15·48	1·746	15·0	345	18	·0307	22	24	—	—	—	—	—	—	

Cadmium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CdCl_2$, 91·37.

·0503	·0055	·9991	18·0	4·6[1]	18	·0231	835	887	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 492.
·0999	·01095	·9996	18·0	8·34	18	·0226	761	809	—	—	—	—	—	—	
·20	·02194	1·0004	18·0	14·5	18	·0231	660	702	—	—	—	—	—	—	
·399	·0439	1·0022	18·0	24·7	18	·0227	563	598	—	—	—	—	—	—	
·518	·057	1·0045	10·5	—	—	—	—	—	·708[2]	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
·599	·066	1·0039	18·0	33·8	18	·0224	512	544	—	—	—	—	—	—	
·769	·0849	1·0057	18·0	41·6	18	·0224	450	478	—	—	·125	1071[4]	25	—	
·997	·1102	1·0075	18·0	49·2	18	·0222	447	475	—	—	·25	1060	25	—	
1·0	·1105	1·0076	18·0	51·1	18	·0222	—	—	—	—	·5	1028	25	—	
1·002	·1100	—	—	—	—	—	—	—	·725	—	1·0	964	25	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 547.
·849	·0937	1·0062	18·0	45·5[2]	18	·0224	486	517	—	—	—	—	—	—	
5·01	·574	1·0437	18·0	155·0	18	·0218	270	287	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
10·04	1·203	1·0923	18·0	225·0	18	·0217	187	199	—	—	—	—	—	—	
14·79	—	—	—	—	—	—	—	—	·744	—	—	—	—	—	
14·94	1·874	1·1436	18·0	262·0	18	·0218	140	149	—	—	—	—	—	—	[5] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
19·8	2·603	1·1984	18·0	277·0	18	·0227	106	112	—	—	—	—	—	—	
22·96	3·12	1·2415	9·5	—	—	—	—	—	·772	—	—	—	—	—	
26·60	3·75	1·2891	9·5	—	—	—	—	—	·779	—	—	—	—	—	
29·97	4·373	1·3302	18·0	262·0	18	·0252	60	64	—	—	—	—	—	—	
33·53	5·10	1·3899	7·0	—	—	—	—	—	·873	—	—	—	—	—	
40·13	6·558	1·4899	18·0	204·0	18	·0291	31	33	—	—	—	—	—	—	
43·76	7·50	1·5657	6·8	—	—	—	—	—	1·014	—	—	—	—	—	
44·06	7·56	1·5681	9·8	—	—	—	—	—	1·016	—	—	—	—	—	
49·51	9·067	1·6697	18·0	131·0	18	·0353	14	15	—	—	—	—	—	—	
·00649	·00071	—	—	—	18	·0241	960[5]	1020	—	—	—	—	—	—	
·01097	·0012	—	—	—	18	·0244	920	978	—	—	—	—	—	—	
·0193	·00211	—	—	—	18	·0236	870	925	—	—	—	—	—	—	
·0471	·00515	—	—	—	18	·0237	780	829	—	—	—	—	—	—	

Cupric Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CuCl_2$, 67·07.

·0063	·00094	—	—	—	18	—	930[1]	989	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0107	·0016	—	—	—	18	—	900	957	—	—	·125	1064[2]	25	—	
·0201	·003	—	—	—	18	—	870	925	—	—	·25	1044	25	—	
·0396	·0059	—	—	—	18	—	860	915	—	—	·5	996	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·0885	·0132	—	—	—	18	—	750	797	—	—	1·0	907	25	—	

Ferrous Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}FeCl_2$, 63·32.

			°		°					°			°		
·0064	·00101	—	—	—	18	—	710[1]	754	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·01583	·0025	—	—	—	18	—	700	744	—	—	—	—	—	—	
·02406	·0038	—	—	—	18	—	680	723	—	—	—	—	—	—	

Nickel Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}NiCl_2$, 64·67.

·00789	·00122	—	—	—	18	·0245	730[1]	776	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00963	·00149	—	—	—	18	·0240	730	776	—	—	·125	1070[2]	25	—	
·01196	·00185	—	—	—	18	—	740	787	—	—	·25	1046	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.
·01875	·0029	—	—	—	18	·0245	730	776	—	—	·5	996	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	907	25	—	

Manganese Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}MnCl_2$, 62·87.

·522	·083	1·0045	9·0	—	—	—	—	—	·682[2]	—	—	—	—	—	[1] Long, *Wied. Annal.* vol. xi. p. 37.
5·0	·831	1·0456	15·0	492[1]	18	·0216	592	629	—	—	—	—	—	—	
10·0	1·733	1·0895	15·0	790	18	·0206	456	485	—	—	·125	1068[3]	25	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 383.
15·0	2·715	1·1378	15·0	987	18	·0202	363	386	—	—	·25	1043	25	—	
20·0	3·785	1·1900	15·0	1061	18	·0206	280	298	—	—	·5	995	25	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
23·22	4·524	1·2275	6·6	—	—	—	—	—	·758	—	1·0	904	25	—	
25·0	4·960	1·2472	15·0	1020	18	·0203	206	219	—	—	—	—	—	—	
28·0	5·710	1·2828	15·0	950	18	·0208	166	176	—	—	—	—	—	—	

Aluminium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}Al_2Cl_6$, 44·37.

·00697	·00157	—	—	—	18	—	830[1]	882	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·00887	·002	—	—	—	18	—	800	850	—	—	—	—	—	—	
·01642	·0037	—	—	—	18	—	806	857	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 391.
4·22	—	—	—	—	—	—	—	—	·714[2]	—	—	—	—	—	

Ferric Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}Fe_2Cl_6$, 54.

·0054	·0010	—	—	—	18	—	2360[1]	2509	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx.
·0108	·0020	—	—	—	18	—	1660	1765	—	—	—	—	—	—	
·0130	·0024	—	—	—	18	—	1510	1605	—	—	—	—	—	—	
·0184	·0034	—	—	—	18	—	1460	1552	—	—	—	—	—	—	
·0286	·0053	—	—	—	18	—	1290	1371	—	—	—	—	—	—	[2] Fitzpatrick, *Phil. Mag.* vol. xxiv. p. 377.
·0324	·0060	—	—	—	18	—	1300	1382	—	—	—	—	—	—	
·0168	·00312	—	—	—	18	—	—	1617[2]	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 389.
·0337	·00625	—	—	—	18	—	—	1496	—	—	—	—	—	—	
·0674	·0125	—	—	—	18	—	—	1356	—	—	—	—	—	—	
·1348	·025	—	—	—	18	—	—	1211	—	—	—	—	—	—	
·2696	·05	—	—	—	18	—	—	1053	—	—	—	—	—	—	
·539	·1	—	—	—	18	—	—	908	—	—	—	—	—	—	
1·078	·2	—	—	—	18	—	—	741[1]	—	—	—	—	—	—	
3·81	—	—	—	—	—	—	—	—	·6[3]	—	—	—	—	—	
32·51	—	—	—	—	—	—	—	—	·746	—	—	—	—	—	

Hydrobromic Acid.

Equivalent Gramme Molecule, HBr, 80·75.

·00195	·000244	—	—	87·8[1]	25	—	—	3559	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 488.
·0039	·000488	—	—	88·9	25	—	—	3612	—	—	—	—	—	—	
·0078	·000976	—	—	89·7	25	—	—	3636	—	—	—	—	—	—	
·0156	·00195	—	—	89·8	25	—	—	3644	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 399.
·0312	·0039	—	—	89·6	25	—	—	3640	—	—	—	—	—	—	
·0625	·0078	—	—	89·4	25	—	—	3632	—	—	—	—	—	—	
·125	·0156	—	—	88·9	25	—	—	3612	—	—	—	—	—	—	
·25	·0312	—	—	87·9	25	—	—	3571	—	—	—	—	—	—	
·502	·0625	1·004	14	86·6	25	—	—	3519	—	—	—	—	—	—	
1·0	·125	1·007	14	85·1	25	—	—	3458	—	—	—	—	—	—	
2·0	·25	1·014	14	83·4	25	—	—	3389	—	—	—	—	—	—	
3·92	·5	1·027	14	80·4	25	·0153	—	3267	—	—	—	—	—	—	
10·36	—	—	—	—	—	—	—	—	·178[2]	—	—	—	—	—	

Potassium Bromide.

Equivalent Gramme Molecule, KBr, 118·79.

			°		°					°			°		
·851	·072	1·0063	7·0	—	—	—	—	—	·514[2]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	·5	—	—	497[1]	18	·0205	994	1057	—	—					
—	1·0	—	—	960	18	·0193	960	1020	—	—	1·309	1013[3]	20	·0217	
—	1·5	—	—	1404	18	·0184	936	995	—	—	2·321	1028	20	·0203	
—	2·0	—	—	1832	18	·0177	916	974	—	—	3·824	999	20	·0179	[2] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
—	2·5	—	—	2243	18	·0171	897	954	—	—	—	—	—	—	
—	3·0	—	—	2623	18	·0166	874	929	—	—	—	—	—	—	
29·7	3·15	1·261	12·2	—	—	—	—	—	·528	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 11.
—	3·5	—	—	2977	18	·0160	850	904	—	—	—	—	—	—	
—	4·0	—	—	3294	18	·0156	824	876	—	—	—	—	—	—	

Cadmium Bromide.

Equivalent Gramme Molecule, $\frac{1}{2}CdBr_2$, 135·75.

·0324	·002386	·9990	18	2·15[1]	18	·0235	899	956	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·0748	·005517	·99935	18	4·37	18	·0237	792	842	—	—	—	—	—	—	
·154	·01134	1·00002	18	7·84	18	·0239	691	735	—	—	—	—	—	—	
·253	·01867	1·0010	18	11·6	18	·0237	623	662	—	—	—	—	—	—	
·506	·03743	1·0031	18	19·8	18	·0238	529	562	—	—	—	—	—	—	
1·013	·07517	1·0075	18	33·3	18	·0233	443	471	—	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
1·01	·0751	1·0073	18	33·4[2]	18	·0232	445	473	—	—	—	—	—	—	
5·07	·390	1·0437	18	101·0	18	·0225	259	275	—	—	—	—	—	—	
10·10	·813	1·0916	18	152·0	18	·0232	187	199	—	—	—	—	—	—	
20·11	1·781	1·2004	18	219·0	18	·0239	123	131	—	—	—	—	—	—	
29·95	2·936	1·3288	18	253·0	18	·0258	86	91·4	—	—	—	—	—	—	
42·99	4·904	1·5464	18	242·0	18	·0288	49	52	—	—	—	—	—	—	

Hydriodic Acid.

Equivalent Gramme Molecule, HI, 127·53.

·0031	·000244	—	—	87·8[1]	25	—	—	3567	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 438.
·0062	·000488	—	—	89·0	25	—	—	3616	—	—	—	—	—	—	
·0123	·000976	—	—	89·3	25	—	—	3628	—	—	—	—	—	—	
·0247	·00195	—	—	89·7	25	—	—	3644	—	—	—	—	—	—	
·0495	·0039	—	—	89·7	25	—	—	3644	—	—	—	—	—	—	

·099	·0078	—	—	89·4	25	—	—	3632	—	—	—	—	—	—
·198	·0156	—	—	88·7	25	—	—	3608	—	—	—	—	—	—
·397	·0312	—	—	87·6	25	—	—	3559	—	—	—	—	—	—
·792	·0625	1·0058	13·5	86·4	25	—	—	3511	—	—	—	—	—	—
·844	—	—	—	—	25	—	—	—	·258[2]	—	—	—	—	—
1·576	·125	1·0117	13·5	84·9	25	·0158	—	3450	—	—	—	—	—	—
3·11	·25	1·0230	13·5	83·2	25	—	—	3381	—	—	—	—	—	—
6·1	·5	1·0453	13·5	80·4	25	—	—	3267	—	—	—	—	—	—
17·17	—	—	—	—	—	—	—	—	·201	—	—	—	—	—

[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 401.

Potassium Iodide.

Equivalent Gramme Molecule, KI, 165·9.

·017	·000976	—	—	143·1[1]	25	—	—	1319	—	—	—	—	—	—
·034	·00195	—	—	139·1	25	—	—	1282	—	—	—	—	—	—
·067	·0039	—	—	136·1	25	—	—	1254	—	—	—	—	—	—
·134	·0078	—	—	132·9	25	—	—	1225	—	—	—	—	—	—
·269	·0156	—	—	129·3	25	—	—	1192	—	—	—	—	—	—
·518	·0312	—	—	125·4	25	—	—	1156	—	—	—	—	—	—
·000166	·00001	—	—	—	18	—	1207[2]	1283	—	—	—	—	—	—
·000332	·00002	—	—	—	18	—	1216	1293	—	—	—	—	—	—
·000995	·00006	—	—	—	18	—	1216	1293	—	—	—	—	—	—
·00166	·0001	—	—	—	18	—	1216	1293	—	—	—	—	—	—
·00332	·0002	—	—	—	18	—	1214	1291	—	—	—	—	—	—
·00996	·0006	—	—	—	18	—	1209	1285	—	—	·541	1009[4]	20	·0242
·0166	·001	—	—	—	18	—	1203	1279	—	—	1·171	1057	20	·0219
·0332	·002	—	—	—	18	—	1197	1273	—	—	2·610	1082	20	·0190
·0996	·006	—	—	—	18	—	1176	1250	—	—	4·119	1046	20	·0170
·166	·01	—	—	—	18	·0219	1161	1234	—	—	5·257	986	20	·0158
·495	·03	—	—	—	18	—	1123	1194	—	—	—	—	—	—
·8255	·05	1·0048	19·5	—	18	—	1102	1172	—	—	—	—	—	—
1·640	·1	1·0112	19·5	—	18	—	1069	1136	—	—	1·0	1066[5]	20	—
7·823	·5	1·0603	19·5	—	18	·0203	997	1060	—	—	—	—	—	—
10·57	·705	1·1081	12·0	—	—	—	—	—	·511[3]	—	—	—	—	—
14·84	1·0	1·1180	19·5	—	18	·0194	968	1029	—	—	—	—	—	—
26·86	2·01	1·2414	11·0	—	—	—	—	—	·512	—	—	—	—	—
36·8	3·0	1·3530	19·5	—	18	·0156	900	957	—	—	—	—	—	—
52·3	5·0	1·5860	19·5	—	18	·0142	770	819	—	—	—	—	—	—

[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.

[2] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.

[3] Hittorf, *Pogg. Annal.* vol. xcviii. p. 29.

[4] Sprung, *Pogg. Annal.* vol. clix. p. 1.

[5] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

Ammonium Iodide.

Equivalent Gramme Molecule, NH_4I, 144·84.

			°		°				°				°		
10·0	·735	1·0652	18	722[1]	18	·0202	982	1044	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
20·0	1·574	1·1397	18	1494	18	·0193	949	1009	—	—	—	—	—	—	
30·0	2·54	1·2260	18	2318	18	·0180	912	969	—	—	—	—	—	—	
40·0	3·663	1·3260	18	3166	18	·0167	867	922	—	—	—	—	—	—	
50·0	4·98	1·4415	18	3917	18	·0154	786	835	—	—	—	—	—	—	

Sodium Iodide.

Equivalent Gramme Molecule, NaI, 149·84.

5·0	·346	1·0374	18	279[1]	18	·0222	806	857	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
10·0	·721	1·0803	18	543	18	·0216	753	801	—	—	—	—	—	—	
20·0	1·567	1·1735	18	1069	18	·0204	682	725	—	—	—	—	—	—	
30·0	2·57	1·2836	18	1545	18	·0198	600	638	—	—	—	—	—	—	
40·0	3·77	1·4127	18	1972	18	·0199	523	556	—	—	—	—	—	—	

Lithium Iodide.

Equivalent Gramme Molecule, LiI, 133·82.

5·0	·387	1·0361	18	277[1]	18	·0219	716	761	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
10·0	·804	1·0756	18	536	18	·0216	666	708	—	—	—	—	—	—	
15·0	1·253	1·1180	18	783	18	·0212	625	665	—	—	—	—	—	—	
20·0	1·740	1·1643	18	1023	18	·0207	588	625	—	—	—	—	—	—	
25·0	2·267	1·2138	18	1258	18	·0203	555	590	—	—	—	—	—	—	

Cadmium Iodide.

Equivalent Gramme Molecule, $\frac{1}{2}CdI_2$, 182·53.

·0429	·00235	·9991	18·0	1·95[1]	18	·0257	829	881	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·1	·0055	·9996	18·0	3·83	18	·0261	696	740	—	—	—	—	—	—	
·204	·0112	1·0005	18·0	6·6	18	·0262	589	626	—	—	—	—	—	—	
·399	·0220	1·0021	18·0	10·7	18	·0264	486	517	—	—	—	—	—	—	
·6	·0330	1·0038	18·0	14·1	18	·0266	427	454	·613[3]	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
·8	·0441	1·0056	18·0	17·0	18	·0270	386	410	—	—	—	—	—	—	
1·0	·0552	1·0072	18·0	19·7	18	·0271	356	378	—	—	—	—	—	—	
1·017	·0562	1·0073	18·0	19·7[2]	18	·0286	350	372	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 543.
1·41	—	—	—	—	—	—	—	—	·642	—	—	—	—	—	

4·87	·278	1·0413	18·0	55·5	18	·0261	200	213	—	—	—	—	—	—	
5·23	·3	1·0456	11·2	—	—	—	—	—	·931	—	—	—	—	—	
10·03	·599	1·0885	18·0	96·6	18	·0248	161	171	—	—	—	—	—	—	
14·67	·913	1·1354	18·0	132·0	18	·0242	144	153	—	—	—	—	—	—	
19·0	1·230	1·1854	11·8	—	—	—	—	—	1·14	—	—	—	—	—	
19·54	1·274	1·1890	18·0	169·0	18	·0240	132	140	—	—	—	—	—	—	
24·75	1·700	1·2551	11·0	—	—	—	—	—	1·192	—	—	—	—	—	
29·6	2·138	1·3171	18·0	234·0	18	·0244	101	107	—	—	—	—	—	—	
35·32	—	—	—	—	—	—	—	—	1·258	—	—	—	—	—	
40·03	3·254	1·4821	18·0	281·0	18	·0254	86	91	—	—	—	—	—	—	
44·13	3·770	1·5576	18·0	290·0	18	·0258	77	82	—	—	—	—	—	—	
47·5	—	—	18·0	293·0	18	·0263	—	—	—	—	—	—	—	—	

Potassium Cadmium Iodide.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CdI_4$, 347·43.

·0328	·00094	·99895	18	1·9[1]	18	·0226	2016	2143	—	—	—	—	—	—	
·0596	·00171	·99921	18	3·32	18	·0231	1935	2057	—	—	—	—	—	—	
·0804	·00231	·99938	18	4·32	18	·0228	1869	1987	—	—	—	—	—	—	
·10	·00287	·99945	18	5·26	18	·0229	1831	1946	—	—	—	—	—	—	
·25	·00719	1·0007	18	11·8	18	·0233	1645	1748	—	—	—	—	—	—	
·50	·01441	1·0027	18	21·6	18	·0231	1498	1592	—	—	—	—	—	—	
1·003	·02923	1·0067	18	38·5	18	·0234	1317	1400	—	—	—	—	—	—	
1·674	—	—	—	—	—	—	—	—	·56[3]	—	—	—	—	—	
1·006	·0291	1·0065	18	38·3[2]	18	·0235	1309	1391	—	—	—	—	—	—	
5·04	·151	1·0387	18	148·0	18	·0227	980	1042	—	—	—	—	—	—	
10·14	·315	1·0821	18	278·0	18	·0224	882	938	—	—	—	—	—	—	
15·11	·490	1·1280	18	408·0	18	·0218	833	885	—	—	—	—	—	—	
25·25	·896	1·2338	18	689·0	18	·0214	769	817	—	—	—	—	—	—	
30·33	—	—	—	—	—	—	—	—	·79	—	—	—	—	—	
34·96	1·362	1·3552	18	986·0	18	·0207	724	770	—	—	—	—	—	—	
45·12	1·957	1·5086	18	1319·0	18	·0198	674	716	—	—	—	—	—	—	

Hydrofluoric Acid.

Equivalent Gramme Molecule, HF, 20·1.

·000488	·000244	—	—	69·42[1]	25	—	—	3134[2]	—	—	—	—	—	—	
·000976	·000488	—	—	59·56	25	—	—	2689	—	—	—	—	—	—	
·00195	·000976	—	—	49·49	25	—	—	2235	—	—	—	—	—	—	
·0039	·00195	—	—	39·11	25	—	—	1765	—	—	—	—	—	—	

[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.

[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.

[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 527.

[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 303.

[2] At 25°.

Hydrofluoric Acid—*continued.*

Equivalent Gramme Molecule, HF, 20·1.

			°		°					°					
·0078	·0039	—	—	30·30	25	—	—	1368	—	—	—	—	—	—	
·0156	·0078	—	—	23·11	25	—	—	1043	—	—	—	—	—	—	
·0312	·0156	—	—	17·38	25	—	—	786	—	—	—	—	—	—	
·0625	·0312	—	—	13·14	25	—	—	594	—	—	—	—	—	—	
·125	·0625	—	—	10·00	25	—	—	451	—	—	—	—	—	—	
·25	·125	—	—	7·89	25	—	—	356	—	—	—	—	—	—	
·5	·25	—	—	6·54	25	—	—	296	—	—	—	—	—	—	

Potassium Fluoride.

Equivalent Gramme Molecule, KF, 58·14.

—	·5	—	—	367[1]	18	—	734	780	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	1·0	—	—	676	18	·0214	676	718	—	—	—	—	—	—	
—	2·0	—	—	1196	18	·0217	598	636	—	—	—	—	—	—	
—	3·0	—	—	1609	18	·0219	536	570	—	—	—	—	—	—	
—	4·0	—	—	1936	18	·0220	484	514	—	—	—	—	—	—	
—	5·0	—	—	2182	18	·0222	436	463	—	—	—	—	—	—	
—	6·0	—	—	2338	18	·0226	390	414	—	—	—	—	—	—	
—	7·0	—	—	2416	18	·0232	345	366	—	—	—	—	—	—	
—	8·0	—	—	2422	18	·0238	303	322	—	—	—	—	—	—	
—	9·0	—	—	2385	18	·0248	265	282	—	—	—	—	—	—	
—	10·0	—	—	2303	18	·0260	230	244	—	—	—	—	—	—	

Nitric Acid.

Equivalent Gramme Molecule, HNO_3, 63·04.

·000063	·00001	—	—	—	18	—	1144[1]	1213	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000126	·00002	—	—	—	18	—	1904	2024	—	—	—	—	—	—	
·00038	·00006	—	—	—	18	—	2863	3043	—	—	—	—	—	—	
·00063	·0001	—	—	—	18	—	3088	3282	—	—	—	—	—	—	
·00126	·0002	—	—	—	18	—	3285	3492	—	—	—	—	—	—	
·00378	·0006	—	—	—	18	—	3408	3622	—	—	—	—	—	—	
·0063	·001	—	—	—	18	—	3427	3643	—	—	—	—	—	—	
·0126	·002	—	—	—	18	—	3448	3665	—	—	—	—	—	—	
·0378	·006	—	—	—	18	—	3421	3636	—	—	—	—	—	—	
·063	·01	—	—	—	18	·0162	3395	3609	—	—	—	—	—	—	

·189	·03	—	—	—	18	—	3328	3537	—	—	1·02	950[2]	20	·0227	[2] Grotian, *Pogg. Annal.* vol. clx. p. 262.
·315	·05	—	—	—	18	—	3289	3497	—	—	2·11	921	20	·0211	
·63	·1	1·0034	15	—	18	—	3225	3428	—	—	3·28	874	20	·0200	
3·09	·5	1·0185	15	—	18	—	2991	3179	—	—	5·865	788	20	·0184	[3] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 439.
6·09	1·0	1·0354	15	—	18	—	2770	2944	—	—	7·24	669	20	·0181	
17·17	3·0	1·1010	15	—	18	—	2070	2200	—	—	—	—	—	—	
22·0	5·0	1·1660	15	—	18	—	1470	1562	—	—	—	—	—	—	
48·26	10·0	1·3061	15	—	18	—	610	648	—	—	—	—	—	—	[4] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00075	·000121	—	—	83·9[3]	25	—	—	3234	—	—	—	—	—	—	
·0015	·000243	—	—	86·7	25	—	—	3432	—	—	—	—	—	—	
·0030	·000487	—	—	88·2	25	—	—	3537	—	—	—	—	—	—	
·0061	·000975	—	—	89·0	25	—	—	3585	—	—	—	—	—	—	
·0122	·00195	—	—	88·9	25	—	—	3591	—	—	—	—	—	—	
·0245	·0039	—	—	88·5	25	—	—	3580	—	—	—	—	—	—	
·049	·0078	—	—	88·4	25	—	—	3574	—	—	—	—	—	—	
·098	·0156	—	—	87·5	25	—	—	3544	—	—	—	—	—	—	
·197	·0312	—	—	86·2	25	—	—	3500	—	—	—	—	—	—	
·393	·0625	1·0017	15	84·9	25	—	—	3443	—	—	—	—	—	—	
·784	·125	1·0044	15	82·7	25	—	—	3358	—	—	—	—	—	—	
1·56	·25	1·0090	15	80·2	25	—	—	3261	—	—	—	—	—	—	
3·09	·5	1·0185	15	77·9	25	—	—	3159	—	—	—	—	—	—	
·396	·063	1·0019	15	20·5[4]	18	—	3254	3459	—	—	—	—	—	—	
·785	·126	1·0046	15	40·3	18	—	3200	3401	—	—	—	—	—	—	
1·57	·252	1·0094	15	78·3	18	—	3103	3298	—	—	—	—	—	—	
3·12	·504	1·0188	15	150·0	18	—	2953	3139	—	—	—	—	—	—	

Potassium Nitrate.

Equivalent Gramme Molecule, KNO_3, 101·17.

·000101	·00001	—	—	—	18	—	1215[1]	1292	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000202	·00002	—	—	—	18	—	1198	1274	—	—	—	—	—	—	
·000607	·00006	—	—	—	18	—	1220	1297	—	—	—	—	—	—	
·00101	·0001	—	—	—	18	—	1207	1283	—	—	·649	993[2]	20	·0246	[2] Sprung, *Pogg. Annal.* vol. clix. p. 12.
·00202	·0002	—	—	—	18	—	1199	1275	—	—	1·3	1008	20	·0225	
·00607	·0006	—	—	—	18	—	1190	1265	—	—	1·943	988	20	·0214	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0101	·001	—	—	—	18	—	1180	1255	—	—	—	—	—	—	
·0202	·002	—	—	—	18	—	1173	1247	—	—	1·0	1018[3]	20	—	
·0607	·006	—	—	—	18	—	1140	1212	—	—	—	—	—	—	

Potassium Nitrate—*continued.*

Equivalent Gramme Molecule, KNO_3, 101·17.

·101	·01	·99988	0 15·0	—	18	·0216	1122	1193	—	—	·125	981[6]	0 20	—	[4] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·303	·03	1·0013	15·0	—	18	—	1067	1134	—	—	·25	986	20	—	
·504	·05	1·0028	15·0	—	18	—	1037	1102	—	—	·5	991	20	—	
1·005	·1	1·0064	15·0	—	18	—	983	1045	—	—	1·0	1003	20	—	[5] Hittorf, *Pogg. Annal.* vol. ciii. p. 41.
1·06	·105	1·0068	8·0	—	—	—	—	—	·497[5]	—	—	—	—	—	
3·08	·31	1·0201	7·0	—	—	—	—	—	·494	—	—	—	—	—	
4·9	·5	1·0314	15·0	—	18	·0209	839	892	—	—	·125	987[7]	20	—	[6] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 87.
9·4	·99	1·0620	11·4	—	—	—	—	—	·487	—	·25	987	20	—	
9·52	1·0	1·0621	15·0	—	18	·0206	752	799	—	—	·5	989	20	—	
17·8	2·1	1·1290	12·0	—	—	—	—	—	·479	—	1·0	994	20	—	
—	3·0	—	—	—	18	·0188	572	608	—	—	—	—	—	—	[7] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
·0099	·000976	—	—	135·9[4]	25	—	—	1255	—	—	—	—	—	—	
·0197	·00195	—	—	132·6	25	—	—	1224	—	—	—	—	—	—	
·0395	·0039	—	—	129·2	25	—	—	1193	—	—	—	—	—	—	[8] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·079	·0078	—	—	125·7	25	—	—	1161	—	—	—	—	—	—	
·158	·0156	—	—	121·6	25	—	—	1123	—	—	—	—	—	—	
·316	·0312	—	—	117·2	25	—	—	1086	—	—	—	—	—	—	
·63	·0625	1·0037	15·0	61·9[8]	18	—	991	1053	—	—	—	—	—	—	
1·254	·125	1·0080	15·0	117·8	18	—	942	1001	—	—	—	—	—	—	
2·49	·25	1·0159	15·0	221·0	18	—	882	937	—	—	—	—	—	—	
4·9	·5	1·0314	15·0	408·0	18	—	816	867	—	—	—	—	—	—	

Ammonium Nitrate.

Equivalent Gramme Molecule, NH_4NO_3, 79·9.

—	·5	—	—	442·0[1]	18	·0206	884	939	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	1·0	—	—	831·0	18	·0199	831	883	—	—	·767[2]	1011	20	·0236	
—	2·0	—	—	1507·0	18	·0187	754	801	—	—	1·606	1018	20	·0223	
—	3·0	—	—	2082·0	18	·0178	694	737	—	—	3·8	1000	20	·0167	
—	4·0	—	—	2561·0	18	·0170	640	680	—	—	5·46	927	20	·0169	[2] Sprung, *Pogg. Annal.* vol. clix. p. 10.
—	5·0	—	—	2929·0	18	·0165	586	623	—	—	7·71	743	20	·0173	
—	6·0	—	—	3190·0	18	·0161	532	565	—	—	—	—	—	—	
—	7·0	—	—	3351·0	18	·0158	479	505	—	—	—	—	—	—	
—	8·0	—	—	3419·0	18	·0157	427	454	—	—	—	—	—	—	

—	·0625	—	—	62·9[3]	18	—	1006	1069	—	—	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·125	—	—	120·1	18	—	961	1021	—	—	—	—	—	—	
—	·25	—	—	227·0	18	—	908	965	—	—	—	—	—	—	
—	·5	—	—	432·7	18	—	865	919	—	—	—	—	—	—	

SODIUM NITRATE.

Equivalent Gramme Molecule, $NaNO_3$, 85·08.

·000085	·00001	—	—	—	18	—	975[1]	1036	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·00017	·00002	—	—	—	18	—	972	1033	—	—	—	—	—	—	
·00051	·00006	—	—	—	18	—	970	1031	—	—	·895	931[5]	20	·0240	
·00085	·0001	—	—	—	18	—	975	1036	—	—	1·58	872	20	·0241	
·0017	·0002	—	—	—	18	—	966	1027	—	—	2·422	801	20	·0234	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·0051	·0006	—	—	—	18	—	956	1016	—	—	4·614	583	20	·0245	
·0085	·001	—	—	—	18	—	952	1013	—	—	—	—	—	—	
·017	·002	—	—	—	18	—	942	1001	—	—	1·0	929[6]	20	—	[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 80.
·051	·006	—	—	—	18	—	921	979	—	—	—	—	—	—	
·085	·01	—	—	—	18	·0226	907	964	—	—	·125	978[7]	20	—	
·255	·03	1·0004	20·2	—	18	—	877	932	—	—	·25	968	20	—	
·424	·05	1·0018	20·2	—	18	—	855	909	—	—	·5	945	20	—	
·77	·091	1·0052	13·0	—	—	—	—	—	·613[4]	—	1·0	893	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 377.
·846	·1	1·0053	20·2	—	18	—	817	868	—	—	—	—	—	—	
1·057	·125	1·0074	10·0	—	—	—	—	—	·615	—	—	—	—	—	
1·72	·204	1·0118	12·0	—	—	—	—	—	·613	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 14.
2·8	·335	1·0195	12·0	—	—	—	—	—	·614	—	—	—	—	—	
4·14	·5	1·0273	20·2	—	18	·0223	694	738	—	—	—	—	—	—	
8·07	1·0	1·0542	20·2	—	18	·0219	617	656	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
22·04	3·0	1·1581	20·2	—	18	·0216	430	457	—	—	—	—	—	—	
25·0	3·5	1·1904	9·2	—	—	—	—	—	·600	—	—	—	—	—	
·53	·0625	1·0026	20·2	52·1[3]	18	—	834	886	—	—	—	—	—	—	[7] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
1·056	·125	1·0067	20·2	98·4	18	—	787	836	—	—	—	—	—	—	
2·1	·25	1·0137	20·2	184·8	18	—	739	785	—	—	—	—	—	—	
4·14	·5	1·0273	20·2	340·0	18	—	680	725	—	—	—	—	—	—	
·0083	·000976	—	—	113·7[3]	25	—	—	1043	—	—	—	—	—	—	
·0166	·00195	—	—	111·2	25	—	—	1020	—	—	—	—	—	—	
·0331	·0039	—	—	108·5	25	—	—	996	—	—	—	—	—	—	
·0662	·0078	—	—	105·6	25	—	—	969	—	—	—	—	—	—	
·1325	·0156	—	—	102·4	25	—	—	940	—	—	—	—	—	—	
·265	·0312	1·0004	20·2	99·0	25	—	—	909	—	—	—	—	—	—	

Lithium Nitrate.

Equivalent Gramme Molecule, $LiNO_3$, 68·9.

			°		°					°				°		
·0067	·000976	—	—	105·1[1]	25	—	—	962	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 88.
·0134	·00195	—	—	102·0	25	—	—	934	—	—	—	—	—	—	
·0268	·0039	—	—	99·0	25	—	—	906	—	—	—	—	—	—	
·0535	·0078	—	—	96·1	25	—	—	880	—	—	—	—	—	—	
·107	·0156	—	—	92·6	25	—	—	848	—	—	—	—	—	—	[2] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
·214	·0312	—	—	89·6	25	—	—	820	—	—	—	—	—	—	
·0134	·00195	—	—	1·65[2]	18	—	844	900	—	—	—	—	—	—	
·0268	·0039	—	—	3·26	18	—	839	889	—	—	—	—	—	—	
·0535	·0078	—	—	6·45	18	—	825	880	—	—	—	—	—	—	
·107	·0156	—	—	12·6	18	—	810	856	—	—	—	—	—	—	
·214	·0312	—	—	24·2	18	—	774	827	—	—	—	—	—	—	
·428	·0625	—	—	46·5	18	—	744	790	—	—	—	—	—	—	
—	·125	—	—	88·5	18	—	708	752	—	—	—	—	—	—	
—	·25	—	—	166·0	18	—	664	707	—	—	—	—	—	—	
—	·5	—	—	303·0	18	—	606	645	—	—	—	—	—	—	
—	1·0	—	—	532·0	18	—	532	550	—	—	—	—	—	—	

Silver Nitrate.

Equivalent Gramme Molecule, $AgNO_3$, 169·9.

·00017	·00001	—	—	—	18	—	1080[1]	1148	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·00034	·00002	—	—	—	18	—	1073	1141	—	—	—	—	—	—	
·00102	·00006	—	—	—	18	—	1077	1145	—	—	—	—	—	—	
·0017	·0001	—	—	—	18	—	1078	1146	—	—	—	—	—	—	
·0034	·0002	—	—	—	18	—	1077	1145	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. lxxxix. p. 203.
·0102	·0006	—	—	—	18	—	1069	1136	—	—	—	—	—	—	
·017	·001	—	—	—	18	—	1068	1135	—	—	·125	1093[3]	25	—	
·034	·002	—	—	—	18	—	1057	1124	—	—	·25	1086	25	—	
·102	·006	—	—	—	18	—	1033	1098	—	—	·5	1071	25	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
·17	·01	—	—	—	18	·0221	1017	1081	—	—	1·0	1033	25	—	
·403	—	1·0044	9·6	—	—	—	—	—	·524[2]	9·6	—	—	—	—	
·507	·03	—	—	—	18	—	966	1027	—	—	—	—	—	—	
·842	·05	1·0070	18·0	—	18	—	936	995	—	—	—	—	—	—	
·947	—	1·0076	18·6	—	—	—	—	—	·526	18·6	—	—	—	—	
1·657	·1	1·0131	18·0	—	18	—	886	942	—	—	—	—	—	—	
1·98	—	1·0166	18·5	—	—	—	—	—	·526	18·5	—	—	—	—	
4·06	—	1·0343	18·4	—	—	—	—	—	·527	18·4	—	—	—	—	

6·45	—.	1·0558	19·2	—	—	—	—	—	·525	19·2	—	—	—	—
7·927	·5	1·0693	18·0	—	18	·0218	728	774	—	—	—	—	—	—
8·772	—	1·0774	18·8	—	—	—	—	—	·510	18·8	—	—	—	—
14·91	1·0	1·1395	18·0	—	18	·0216	635	675	—	—	—	—	—	—
16·18	—	1·1534	18·4	—	—	—	—	—	·495	18·4	—	—	—	—
26·81	—	1·2788	19·2	—	—	—	—	—	·478	19·0	—	—	—	—
28·73	—	1·3079	11·1	—	—	—	—	—	·468	11·2	—	—	—	—
36·11	3·0	1·4120	18·0	—	18	·0207	448	476	—	—	—	—	—	—
50·44	5·0	1·6843	18·0	—	18	·0206	351	373	—	—	—	—	—	—
·0136	·0008	—	—	1232[4]	25	—	—	1134	—	—	—	—	—	—
·0255	·0015	—	—	1221	25	—	—	1124	—	—	—	—	—	—
·051	·003	—	—	1206	25	—	—	1110	—	—	—	—	—	—
·119	·007	—	—	1188	25	·0222	—	1094	—	—	—	—	—	—
·178	·0105	—	—	—	—	—	—	—	·524[4]	26·0	—	—	—	—
·255	·015	—	—	1153	25	—	—	1061	—	—	—	—	—	—
·42	·025	—	—	1126	25	·0217	—	1037 {	·522	26·0	—	—	—	—
									·538	0·0	—	—	—	—
·842	·05	1·007	18·0	1086	25	—	—	1000	—	—	—	—	—	—
—	·052	—	—	—	—	—	—	—	·524	26·0	—	—	—	—
1·657	·1	1·0131	18·0	1022	25	·0213	—	941	—	—	—	—	—	—
—	·104	—	—	—	—	—	—	—	·528	20·0	—	—	—	—
·00763	·00045	—	—	—	18	·0228	1040[5]	1105	—	—	—	—	—	—
·00915	·00054	—	—	—	18	·0229	1030	1095	—	—	—	—	—	—
·0166	·00097	—	—	—	18	·0227	1010	1074	—	—	—	—	—	—
·0410	·00242	—	—	—	18	—	990	1052	—	—	—	—	—	—

STRONTIUM NITRATE.

Equivalent Gramme Molecule, $\frac{1}{2}Sr(NO_3)_2$, 105·54.

5·0	·494	1·0418	15	289[1]	18	·0225	585	622	—	—	·125	1080[2]	25	—
10·0	1·029	1·0857	15	493	18	·0225	479	509	—	—	·25	1067	25	—
15·0	1·608	1·1318	15	645	18	·0227	401	426	—	—	·5	1042	25	—
20·0	2·240	1·1815	15	750	18	·0228	335	356	—	—	1·0	980	25	—
25·0	2·929	1·2363	15	810	18	·0226	277	294	—	—	—	—	—	—
35·0	4·490	1·3542	15	805	18	·0241	179	190	—	—	—	—	—	—
·00918	·00087	—	—	—	18	—	980[2]	1042	—	—	·125	961[4]	20	—
·01076	·00102	—	—	—	18	—	990	1052	—	—	·25	931	20	—
·01604	·00152	—	—	—	18	—	950	1010	—	—	·5	878	20	—
·03747	·00355	—	—	—	18	—	920	978	—	—	1·0	777	20	—

[4] Loeb and Nernst, *Zeitschrift für physik. Chemie*, vol. ii. p. 956.

[5] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.

[1] Long, *Wied. Annal.* vol. xi. p. 37.

[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.

[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.

[4] Mutzel, *Wied. Annal.* vol. xliii. p. 21.

Barium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ba(NO_3)_2$, 130·54.

			°		°					°			°		
·00013	·00001	—	—	—	18	—	1114[1]	1185	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000261	·00002	—	—	—	18	—	1114	1185	—	—	—	—	—	—	
·000783	·00006	—	—	—	18	—	1100	1170	—	—	—	—	—	—	
·0013	·0001	—	—	—	18	—	1096	1165	—	—	·125	1084[4]	25	—	
·00261	·0002	—	—	—	18	—	1084	1152	—	—	·25	1070	25	—	[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·00783	·0006	—	—	—	18	—	1066	1133	—	—	·5	1047	25	—	
·013	·001	—	—	—	18	—	1054	1121	—	—	—	—	—	—	
·0261	·002	—	—	—	18	—	1033	1098	—	—	—	—	—	—	
·0783	·006	—	—	—	18	—	982	1044	—	—	·125	962[5]	20	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.
·1305	·01	—	—	—	18	·0224	951	1011	—	—	·25	938	20	—	
·391	·03	—	—	—	18	—	870	925	—	—	—	—	—	—	
·648	·05	1·0052	19·5	—	18	—	828	880	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 35.
·743	·057	1·0060	10·6	—	—	—	—	—	·602[3]	—	—	—	—	—	
1·29	·1	1·0113	19·5	—	18	—	755	802	—	—	—	—	—	—	
1·74	·135	1·0146	13·6	—	—	—	—	—	·620	—	—	—	—	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
5·8	·466	1·0502	8·0	—	—	—	+	—	·641	—	—	—	—	—	
6·20	·5	1·0520	19·5	—	18	·0241	531	564	—	—	—	—	—	—	
·00665	·00051	—	—	—	18	—	1010[2]	1073	—	—	—	—	—	—	
·0137	·00105	—	—	—	18	—	1000	1063	—	—	—	—	—	—	
·0249	·00191	—	—	—	18	—	980	1042	—	—	—	—	—	—	

Calcium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ca(NO_3)_2$, 82·04.

3·98	·5	1·0307	18·0	314·0[1]	18	·0219	628	668	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
7·73	1·0	1·0608	18·0	541·0	18	·0219	541	575	—	—	—	—	—	—	
14·64	2·0	1·1202	18·0	818·0	18	·0217	409	435	—	—	—	—	—	—	
20·9	3·0	1·1781	18·0	946·0	18	·0217	315	335	—	—	·125	1092[2]	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 86.
26·57	4·0	1·2352	18·0	983·0	18	·0220	246	261	—	—	·25	1069	25	—	
—	5·0	—	—	946·0	18	·0230	189	201	—	—	·5	1038	25	—	
—	6·0	—	—	845·0	18	·0250	141	150	—	—	1·0	978	25	—	
—	7·0	—	—	716·0	18	·0275	102	108	—	—	—	—	—	—	
—	8·0	—	—	584·0	18	·0302	73	78	—	—	—	—	—	—	
—	9·0	1·4984	18·0	461·0	18	·0331	51	54	—	—	—	—	—	—	
—	10·0	—	—	355·0	18	·0363	35	37	—	—	—	—	—	—	
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

·0255	·00312	—	—	30·34[3]	18	—	971	1032	—	—	·125	961[5]	20	—	[3] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
·051	·00625	—	—	57·87	18	—	925	988	—	—	·25	927	20	—	
·102	·0125	—	—	112·2	18	—	898	955	—	—	·5	867	20	—	
·203	·025	—	—	209·6	18	—	838	891	—	—	1·0	766	20	—	
·407	·05	—	—	395·5	18	—	791	841	—	—	—	—	—	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.
·814	·1	1·0069	18·0	730·0	18	—	730	776	—	—	—	—	—	—	
·9	·11	1·0070	7·4	—	—	—	—	—	·613[4]	—	—	—	—	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
1·62	·2	1·0135	18·0	1324·0	18	—	662	704	—	—	—	—	—	—	
20·16	2·88	1·1767	7·4	—	—	—	—	—	·652	—	—	—	—	—	
41·32	7·15	1·3919	7·6	—	—	—	—	—	·718	—	—	—	—	—	

Magnesium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Mg(NO_3)_2$, 74·04.

3·612	·5	1·0249	21	309·0[1]	18	·0218	618	657	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
7·052	1·0	1·0499	21	546·0	18	·0215	546	580	—	—	—	—	—	—	
13·47	2·0	1·0994	21	890·0	18	·0211	445	473	—	—	·125	1072[2]	25	—	
19·34	3·0	1·1482	21	1096·0	18	·0207	365	388	—	—	·25	1051	25	—	[2] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
									—	—	·5	1010	25	—	
·0116	·00156	—	—	12·68[2]	18	—	811	862	—	—	1·0	934	25	—	
·0232	·00312	—	—	25·0	18	—	800	850	—	—	—	—	—	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·0465	·00625	—	—	48·7	18	—	779	828	—	—	·125	944[4]	20	—	
·093	·0125	—	—	93·4	18	—	747	794	—	—	·25	907	20	—	
·185	·025	—	—	182·4	18	—	730	776	—	—	·5	840	20	—	
·37	·05	—	—	343·5	18	—	687	730	—	—	1·0	720	20	—	
·737	·1	1·0051	21	643·6	18	—	644	685	—	—	—	—	—	—	[4] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
1·465	·2	1·0099	21	1200·0	18	—	600	638	—	—	—	—	—	—	

Cadmium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Cd(NO_3)_2$, 117·9.

·0492	·00418	·9990	18	3·95[1]	18	·0234	935	994	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·1	·00849	·9994	18	7·59	18	·0233	894	950	—	—	·125	1074[3]	25	—	
·249	·02123	1·0007	18	18·1	18	·0227	853	907	—	—	·25	1052	25	—	
·464	·03951	1·0025	18	32·5	18	·0230	823	875	—	—	·5	1017	25	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
·952	·08146	1·0065	18	62·7	18	·0222	769	817	—	—	1·0	938	25	—	
1·014	·0868	1·0070	18	65·2[2]	18	·0226	751	798	—	—	—	—	—	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
5·02	·444	1·0416	18	270·0	18	·0221	608	646	—	—	—	—	—	—	
10·07	·930	1·0875	18	480·0	18	·0215	516	548	—	—	—	—	—	—	

Cadmium Nitrate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}Cd(NO_3)_2$, 117·9.

			°		°				°			°		
20·2	2·047	1·1926	18	773·0	18	·0212	377	401	—	—	—	—	—	
30·0	3·345	1·3124	18	891·0	18	·0214	266	283	—	—	—	—	—	
40·0	4·957	1·4589	18	841·0	18	·0228	169	179	—	—	—	—	—	
48·3	6·580	1·6034	18	697·0	18	·0253	106	113	—	—	—	—	—	

Lead Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Pb(NO_3)_2$, 165·1.

·0081	·00049	—	—	—	—	·0231	1100[1]	1169	—	—	—	—	—	
·0125	·00076	—	—	—	—	—	1060	1127	—	—	—	—	—	
·0248	·0015	—	—	—	—	—	1010	1074	—	—	—	—	—	
5·0	·317	1·0449	15	179[2]	18	·0238	565	601	—	—	·125	1086[2]	25	—
10·0	·663	1·0937	15	301	18	·0251	454	483	—	—	·25	1074	25	—
15·0	1·042	1·1467	15	401	18	·0251	385	409	—	—	·5	1049	25	—
20·0	1·460	1·2043	15	487	18	·0250	334	355	—	—	1·0	993	25	—
25·0	1·920	1·2678	15	561	18	·0252	292	310	—	—	—	—	—	—
30·0	2·427	1·3358	15	625	18	·0257	216	230	—	—	—	—	—	—

Chloric Acid.

Equivalent Gramme Molecule, $HClO_3$, 84·25.

·0082	·000976	—	—	384·8[1]	25	—	—	4090[2]	—	—	—	—	—	
·0165	·00195	—	—	381·5	25	—	—	4055	—	—	—	—	—	
·033	·0039	—	—	377·0	25	—	—	4087	—	—	—	—	—	
·066	·0078	—	—	371·0	25	—	—	3944	—	—	—	—	—	
·132	·0156	—	—	363·8	25	—	—	3867	—	—	—	—	—	
·262	·0312	—	—	355·4	25	—	—	3778	—	—	—	—	—	

Potassium Chlorate.

Equivalent Gramme Molecule, $KClO_3$, 122·59.

·000122	·00001	—	—	—	18	—	1141[1]	1213	—	—	—	—	—	
·000245	·00002	—	—	—	18	—	1135	1206	—	—	—	—	—	
·000735	·00006	—	—	—	18	—	1126	1197	—	—	—	—	—	
·00122	·0001	—	—	—	18	—	1122	1193	—	—	—	—	—	
·00245	·0002	—	—	—	18	—	1119	1190	—	—	—	—	—	

[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.

[2] Long, *Wied. Annal.* vol. xi. p. 37.

[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 86.

[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 75.

[2] At 25°.

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.

·00735	·0006	—	—	—	18	—	1109	1179	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 375.
·01226	·001	—	—	—	18	—	1101	1171	—	—	—	—	—	—	
·0245	·002	—	—	—	18	—	1091	1160	—	—	—	—	—	—	
·0735	·006	—	—	—	18	—	1068	1135	—	—	—	—	—	—	[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·1226	·01	—	—	—	18	·0219	1053	1120	—	—	—	—	—	—	
·367	·03	—	—	—	18	—	1006	1069	—	—	—	—	—	—	
·609	·05	—	—	—	18	—	976	1037	—	—	—	—	—	—	
·86	—	—	—	—	—	—	—	—	·462[2]	—	—	—	—	—	
1·215	·1	1·0085	19·5	—	18	—	927	985	—	—	—	—	—	—	
3·62	—	—	—	—	—	—	—	—	·445	—	—	—	—	—	
5·903	·5	1·0384	19·5	—	18	·0212	799	849	—	—	—	—	—	—	
·012	·000976	—	—	130·2[3]	25	—	—	1200	—	—	—	—	—	—	
·024	·00195	—	—	126·8	25	—	—	1169	—	—	—	—	—	—	
·048	·0039	—	—	123·3	25	—	—	1136	—	—	—	—	—	—	
·096	·0078	—	—	120·0	25	—	—	1106	—	—	—	—	—	—	
·191	·0156	—	—	116·6	25	—	—	1075	—	—	—	—	—	—	
·382	·0312	—	—	112·5	25	—	—	1037	—	—	—	—	—	—	

Sodium Chlorate.

Equivalent Gramme Molecule, $NaClO_3$, 106·5.

—	—	—	—	—	—	—	—	—	—	—	1·168[3]	891	20	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0104	·000976	—	—	106·6[1]	25	—	—	1133[2]	—	—	2·23	785	20	—	
·0208	·00195	—	—	104·1	25	—	—	1106	—	—	3·992	586	20	—	
·0415	·0039	—	—	101·5	25	—	—	1079	—	—	—	—	—	—	[2] At 25°.
·0825	·0078	—	—	98·6	25	—	—	1048	—	—	—	—	—	—	
·165	·0156	—	—	95·8	25	—	—	1018	—	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. cvi. p. 15.
·331	·0312	—	—	92·7	25	—	—	985	—	—	—	—	—	—	

Lithium Chlorate.

Equivalent Gramme Molecule, $LiClO_3$, 90·48.

·00877	·000976	—	—	97·0[1]	25	—	—	1031[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 83.
·01755	·00195	—	—	94·2	25	—	—	1001	—	—	—	—	—	—	
·0351	·0039	—	—	91·9	25	—	—	977	—	—	—	—	—	—	
·0702	·0078	—	—	89·1	25	—	—	947	—	—	—	—	—	—	[2] At 25°.
·1405	·0156	—	—	86·4	25	—	—	918	—	—	—	—	—	—	
·281	·0312	—	—	83·7	25	—	—	890	—	—	—	—	—	—	

Perchloric Acid.

Equivalent Gramme Molecule, $HClO_4$, 100·46.

·00976	·000976	—	—	395·5[1]	25	—	—	4204[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·00195	·00195	—	—	391·0	25	—	—	4156	—	—	—	—	—	—	
·039	·0039	—	—	384·8	25	—	—	4090	—	—	—	—	—	—	
·078	·0078	—	—	378·0	25	—	—	4018	—	—	—	—	—	—	
·156	·0156	—	—	369·5	25	—	—	3928	—	—	—	—	—	—	[2] At 25°.
·313	·0312	—	—	361·2	25	—	—	3840	—	—	—	—	—	—	

Potassium Perchlorate.

Equivalent Gramme Molecule, $KClO_4$, 138·59.

·0135	·000976	—	—	139·8[1]	25	—	—	1486[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·027	·00195	—	—	136·4	25	—	—	1450	—	—	—	—	—	—	
·054	·0039	—	—	132·8	25	—	—	1412	—	—	—	—	—	—	
·108	·0078	—	—	129·2	25	—	—	1373	—	—	—	—	—	—	[2] At 25°.
·216	·0156	—	—	124·8	25	—	—	1327	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 378.
·431	·0312	—	—	120·7	25	—	—	1283	—	—	—	—	—	—	
·833	—	—	—	—	—	—	—	—	·463[3]	—	—	—	—	—	

Sodium Perchlorate.

Equivalent Gramme Molecule, $NaClO_4$, 122·5.

·0119	·000976	—	—	116·1[1]	25	—	—	1234[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0238	·00195	—	—	113·3	25	—	—	1204	—	—	—	—	—	—	
·0475	·0039	—	—	110·8	25	—	—	1178	—	—	—	—	—	—	
·095	·0078	—	—	108·2	25	—	—	1150	—	—	—	—	—	—	
·19	·0156	—	—	105·2	25	—	—	1118	—	—	—	—	—	—	[2] At 25°.
·38	·0312	—	—	102·0	25	—	—	1084	—	—	—	—	—	—	

Lithium Perchlorate.

Equivalent Gramme Molecule, $LiClO_4$, 106·48.

·0104	·000976	—	—	107·4[1]	25	—	—	1142	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0208	·00195	—	—	104·4	25	—	—	1119[2]	—	—	—	—	—	—	
·0415	·0039	—	—	101·6	25	—	—	1080	—	—	—	—	—	—	
·083	·0078	—	—	98·9	25	—	—	1051	—	—	—	—	—	—	
·166	·0156	—	—	95·9	25	—	—	1019	—	—	—	—	—	—	[2] At 25°.
·331	·0312	—	—	92·9	25	—	—	987	—	—	—	—	—	—	

Sulphuric Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SO_4$, 49·035.

·000049	·00001	—	—	—	18	—	1413[1]	1502	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000098	·00002	—	—	—	18	—	2077	2208	—	—	—	—	—	—	
·000294	·00006	—	—	—	18	—	2927	3111	—	—	—	—	—	—	
·00049	·0001	—	—	—	18	—	3118	3314	—	—	—	—	—	—	
·00098	·0002	—	—	—	18	—	3280	3486	—	—	·125[4]	927	18	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00294	·0006	—	—	—	18	—	3342	3552	—	—	·25	914	18	—	
·0049	·001	—	—	—	18	—	3316	3524	—	—	·5	895	18	—	
·0098	·002	—	—	—	18	·0159	3240	3444	—	—	1·0	857	18	—	
·0294	·006	—	—	—	18	—	3001	3190	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 401.
·049	·01	—	—	—	18	·0125	2855	3035	—	—	—	—	—	—	
·147	·03	—	—	—	18	—	2515	2673	—	—	—	—	—	—	
·245	·05	—	—	—	18	—	2343	2490	—	—	2·176[5]	756	18	·0249	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
·489	·1	1·0027	15	—	18	—	2084	2215	—	—	4·522	603	18	·0237	
·616	—	—	—	—	—	—	—	—	·206[3]	—	7·438	457	18	·0258	
1·01	—	—	—	—	—	—	—	—	·212	—	10·61	344	18	·0249	[5] Grotian, *Wied. Annal.* vol. viii. p. 543.
2·414	·5	1·0155	15	—	18	—	1899	2018	—	—	14·33	242	18	·0242	
4·1	—	—	—	—	—	—	—	—	·177	—	18·25	160	18	·0259	
4·758	1·0	1·0304	15	—	18	—	1820	1935	—	—	23·17	86	18	·0302	
13·44	3·0	1·0941	15	—	18	—	1560	1658	—	—	29·28	37	18	·0423	
15·59	—	—	—	—	—	—	—	—	·174	—	30·8	34	18	·0432	
21·25	5·0	1·1534	15	—	18	—	1270	1350	—	—	32·18	34	18	·0421	
38·03	10·0	1·2894	15	—	18	—	660	701	—	—	—	—	—	—	
41·0	—	—	—	—	—	—	—	—	·288	—	—	—	—	—	
64·22	—	—	—	—	—	—	—	—	·4	—	—	—	—	—	
·098	·02	—	—	51·9[2]	18	—	2595	2758	—	—	—	—	—	—	
·196	·04	—	—	95·3	18	—	2382	2532	—	—	—	—	—	—	
·391	·08	1·0020	15	175·6	18	—	2195	2333	—	—	—	—	—	—	
·78	·16	1·0048	15	326·9	18	—	2043	2171	—	—	—	—	—	—	
1·553	·32	1·0100	15	613·8	18	—	1918	2038	—	—	—	—	—	—	

Potassium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2SO_4$, 87·16.

·000087	·00001	—	—	—	18	—	1275[1]	1355	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000174	·00002	—	—	—	18	—	1266	1346	—	—	—	—	—	—	
·000523	·00006	—	—	—	18	—	1254	1333	—	—	—	—	—	—	

Potassium Sulphate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}K_2SO_4$, 87·16.

			°		°					°			°		
·00087	·0001	—	—	—	18	—	1249	1328	—	—	·618	916[5]	20	·0244	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00174	·0002	—	—	—	18	—	1241	1319	—	—	1·209	861	20	·0235	
·00523	·0006	—	—	—	18	—	1220	1297	—	—	—	—	—	—	
·0087	·001	—	—	—	18	—	1207	1283	—	—	—	—	—	—	
·0174	·002	—	—	—	18	—	1181	1256	—	—	1·0	888[6]	20	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0523	·006	—	—	—	18	—	1130	1201	—	—	—	—	—	—	
·0871	·01	—	—	—	18	·0223	1098	1167	—	—	·125	966[7]	20	—	
·241	·028	1·0020	6·6	—	—	—	—	—	·498[4]	—	·25	954	20	—	
·261	·03	1·0015	15·0	—	18	—	1008	1071	—	—	·5	928	20	—	[4] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
·434	·05	1·0030	15·0	—	18	—	959	1019	—	—	1·0	883	20	—	
·866	·1	1·0069	15·0	—	18	—	897	954	—	—	—	—	—	—	
4·212	·5	1·0345	15·0	—	18	·0218	736	782	—	—	—	—	—	—	
7·67	·936	1·0639	12·0	—	—	—	—	—	·499	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 16.
8·163	1·0	1·0677	15·0	—	18	·0209	672	714	—	—	—	—	—	—	
·542	·0625	1·0040	15·0	57·0[2]	18	—	912	969	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·629	·0725	1·0047	15·0	65·5	18	—	903	960	—	—	—	—	—	—	
1·080	·125	1·0088	15·0	106·0	18	—	848	899	—	—	—	—	—	—	
1·251	·145	1·0102	15·0	121·0	18	—	834	889	—	—	—	—	—	—	
2·477	·29	1·0202	15·0	223·0	18	—	769	817	—	—	—	—	—	—	
4·212	·5	1·0345	15·0	361·0	18	—	722	767	—	—	—	—	—	—	[7] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·00558	·00064	—	—	—	18	·c238	1250[3]	1329	—	—	—	—	—	—	
·0074	·00085	—	—	—	18	·0237	1210	1286	—	—	—	—	—	—	
·0135	·00155	—	—	—	18	·0239	1160	1233	—	—	—	—	—	—	
·0286	·00325	—	—	—	18	·0231	1090	1159	—	—	—	—	—	—	
·0862	·0099	—	—	—	18	·0223	1020	1084	—	—	—	—	—	—	

Ammonium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2SO_4$, 66·075.

3·236	·5	1·0186	15	351[1]	18	·0221	702	746	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
6·360	1·0	1·0366	15	643	18	·0212	643	683	—	—	—	—	—	—	
12·312	2·0	1·0708	15	1130	18	·0201	565	601	—	—	1·282	853[8]	20	·0238	
17·926	3·0	1·1032	15	1535	18	·0195	512	544	—	—	2·637	745	20	·0229	
—	4·0	—	—	1856	18	·0193	464	493	—	—	4·438	600	20	·0231	

28·336	5·0	1·1632	15	2087	18	·0192	417	443	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	6·0	—	—	2233	18	·0193	372	395	—	—	—	—	—	—	
·411	·0625	1·0018	15	56[2]	18	—	896	952	—	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 16.
·820	·125	1·0045	15	103	18	—	824	876	—	—	—	—	—	—	
1·632	·25	1·0095	15	190	18	—	760	808	—	—	—	—	—	—	
3·236	·5	1·0186	15	347	18	—	694	738	—	—	—	—	—	—	

Sodium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2SO_4$, 71·075.

·000071	·00001	—	—	—	18	—	1054[1]	1121	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000142	·00002	—	—	—	18	—	1056	1123	—	—	—	—	—	—	
·000426	·00006	—	—	—	18	—	1038	1103	—	—	—	—	—	—	
·00071	·0001	—	—	—	18	—	1034	1099	—	—	·485	880[5]	20	·0255	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00142	·0002	—	—	—	18	—	1026	1091	—	—	·989	795	20	·0247	
·00426	·0006	—	—	—	18	—	1009	1072	—	—	1·996	630	20	·0257	
·0071	·001	—	—	—	18	—	998	1060	—	—	—	—	—	—	
·0142	·002	—	—	—	18	—	980	1042	—	—	1·0	796[6]	20	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0426	·006	—	—	—	18	—	933	992	—	—	—	—	—	—	
·071	·01	—	—	—	18	·0240	906	963	—	—	·125	948[7]	20	—	
·213	·03	—	—	—	18	·0240	828	880	—	—	·25	922	20	—	
·355	·05	—	—	—	18	—	784	833	—	—	·5	877	20	—	
·706	·1	1·0062	15	—	18	—	734	780	—	—	1·0	789	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 377.
1·93	·276	1·0181	9	—	—	—	—	—	·634[4]	—	—	—	—	—	
3·542	·5	1·0317	15	—	18	·0232	559	594	—	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 15.
6·70	1·0	1·0612	15	—	18	·0242	475	505	—	—	—	—	—	—	
7·83	1·18	1·0735	9	—	—	—	—	—	·641	—	—	—	—	—	
12·70	2·0	1·1190	15	—	18	·0254	376	400	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·444	·0625	—	—	46·7[2]	18	—	747	794	—	—	—	—	—	—	
·881	·125	1·0080	15	85·5	18	—	684	727	—	—	—	—	—	—	
1·750	·25	1·0158	15	154·0	18	—	616	654	—	—	—	—	—	—	
3·542	·5	1·0317	15	272·0	18	—	544	578	—	—	—	—	—	—	[7] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.
·00604	·00085	—	—	—	18	—	1010[8]	1074	—	—	—	—	—	—	
·00974	·00137	—	—	—	18	—	970	1031	—	—	—	—	—	—	
·01834	·00258	—	—	—	18	—	940	999	—	—	—	—	—	—	

Lithium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Li_2SO_4$, 55·05.

			°		°					°			°		
·000055	·00001	—	—	—	18	—	949[1]	1008	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·00011	·00002	—	—	—	18	—	950	1009	—	—	—	—	—	—	
·00033	·00006	—	—	—	18	—	950	1009	—	—	—	—	—	—	
·00055	·0001	—	—	—	18	—	945	1004	—	—	—	—	—	—	
·0011	·0002	—	—	—	18	—	937	996	—	—	1·0	712[3]	17·6	—	[2] Kuschel, *Wied. Annal.* vol. xiii. p. 300.
·0033	·0006	—	—	—	18	—	918	976	—	—	—	—	—	—	
·0055	·001	—	—	—	18	—	906	963	—	—	—	—	—	—	
·011	·002	—	—	—	18	—	885	941	—	—	·125	1059[4]	25·0	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·033	·006	—	—	—	18	—	844	897	—	—	·25	1026	25·0	—	
·055	·01	—	—	—	18	·0242	818	870	—	—	·5	961	25·0	—	
·165	·03	—	—	—	18	—	742	789	—	—	1·0	847	25·0	—	
·275	·05	—	—	—	18	—	701	745	—	—	—	—	—	—	
—	·09	—	—	—	—	—	—	—	·595[2]	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
·548	·1	—	—	—	18	—	637	677	—	—	—	—	—	—	
—	·159	—	—	—	—	—	—	—	·649	—	—	—	—	—	
2·7	·5	—	—	—	18	·0236	474	504	—	—	—	—	—	—	
5·27	1·0	1·0445	18·6	—	18	·0237	386	410	—	—	—	—	—	—	
—	2·0	—	—	—	18	·0240	287	305	—	—	—	—	—	—	

Silver Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Ag_2SO_4$, 155·9.

·0071	·00046	—	—	—	18	—	1090[1]	1159	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0124	·00080	—	—	—	18	—	1050	1116	—	—	—	—	—	—	
·0263	·00169	—	—	—	18	—	1010	1073	—	—	—	—	—	—	
·0473	·00344	—	—	—	18	—	970	1031	—	—	—	—	—	—	

Magnesium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}MgSO_4$, 60·035.

·00006	·00001	—	—	—	18	—	1056[1]	1123	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·00012	·00002	—	—	—	18	—	1052	1119	—	—	—	—	—	—	
·00036	·00006	—	—	—	18	—	1036	1101	—	—	—	—	—	—	
·0006	·0001	—	—	—	18	—	1034	1099	—	—	—	—	—	—	
·0012	·0002	—	—	—	18	—	1015	1079	—	—	·8715	746[2]	20	·0258	[2] Sprung, *Pogg. Annal.* vol. clix. p. 19.
·0036	·0006	—	—	—	18	—	967	1028	—	—	1·738	554	20	·0283	

·006	·001	—	—	—	18	—	935	994	—	—	2·69	393	20	·0306	[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 109.
·012	·002	—	—	—	18	—	881	937	—	—	3·9	249	20	·0332	
·036	·006	—	—	—	18	—	773	822	—	—	—	—	—	—	
·06	·01	—	—	—	18	·0236	715	760	—	—	1·0	711[5]	20	—	
·18	·03	—	—	—	18	—	587	624	—	—	—	—	—	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 382.
·299	·05	1·0025	15·0	—	18	—	532	565	—	—	·125	937[6]	20	—	
·475	·0795	1·0048	4·8	—	—	—	—	—	·656[4]	—	·25	896	20	—	
·597	·1	1·0058	15·0	—	18	—	474	504	—	—	·5	831	20	—	[5] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
2·912	·5	1·0300	15·0	—	18	·0222	330	351	—	—	1·0	701	20	—	
5·67	1·0	1·0587	15·0	—	18	·0229	270	287	—	—	—	—	—	—	
15·43	3·0	1·1673	15·0	—	18	·0254	151	160	—	—	—	—	—	—	
15·92	3·12	1·1763	3·6	—	—	—	—	—	·762	—	—	—	—	—	[6] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
·00575	·000976	—	—	1133[3]	25	—	—	1023	—	—	—	—	—	—	
·0117	·00195	—	—	1055	25	—	—	952	—	—	—	—	—	—	
·0234	·0039	—	—	966	25	—	—	876	—	—	—	—	—	—	
·0468	·0078	—	—	869	25	—	—	790	—	—	—	—	—	—	
·0935	·0156	—	—	772	25	—	—	703	—	—	—	—	—	—	
·187	·0312	—	—	678	25	—	—	618	—	—	—	—	—	—	

Zinc Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}ZnSO_4$, 80·58.

·00008	·00001	—	—	—	18	—	1060[1]	1127	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000161	·00002	—	—	—	18	—	1047	1113	—	—	—	—	—	—	
·000483	·00006	—	—	—	18	—	1032	1097	—	—	—	—	—	—	
·0008	·0001	—	—	—	18	—	1023	1088	—	—	·0625	946[2]	20	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 385.
·00161	·0002	—	—	—	18	—	1001	1064	—	—	·125	925	20	—	
·00483	·0006	—	—	—	18	—	953	1013	—	—	·25	886	20	—	
·008	·001	—	—	—	18	—	919	977	—	—	·5	817	20	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
·0161	·002	—	—	—	18	—	861	915	—	—	1·0	701	20	—	
·0483	·006	—	—	—	18	—	744	791	—	—	—	—	—	—	
·08	·01	—	—	—	18	·0234	685	728	—	—	1·0	723[4]	20	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·242	·03	—	—	—	18	—	556	591	—	—	—	—	—	—	
·373	—	—	—	—	—	—	—	—	·636[2]	—	·986	708[5]	20	·028	
·4	·05	1·0041	15	—	18	—	500	530	—	—	1·537	595	20	·0297	[5] Grotian, *Pogg. Annal.* vol. clx. p. 263.
·799	·1	1·0090	15	—	18	—	431	458	—	—	2·144	478	20	·0313	
3·85	·5	1·0404	15	—	18	·0226	302	321	—	—	2·993	349	20	·0341	

ZINC SULPHATE—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}ZnSO_4$, 80·58.

7·456	1·0	1·0807	15	—	18	·0224	249	265	—	—	3·555	284	20	·0338	[6] Bouty, *Journ. de Physique*, vol. vi. p. 13.
19·637	3·0	1·2310	15	—	18	·0241	146	155	—	—	5·085	161	20	·0384	
19·8	—	—	—	—	—	—	—	—	·760	—	—	—	—	—	
28·38	—	—	—	—	—	—	—	—	·778	—	—	—	—	—	
29·36	5·0	1·372	15	—	18	·0277	82	87	—	—	—	—	—	—	[7] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·008	·001	—	—	1·02[6]	18	—	—	980	—	—	—	—	—	—	
·080	·01	—	—	7·38	18	—	—	734	—	—	—	—	—	—	[8] Beetz, *Pogg. Annal.* vol. cxvii. p. 9.
·799	·1	1·0090	15	46·46	18	—	—	466	—	—	—	—	—	—	
1·583	·2	1·0179	15	77·3	18	—	—	386	—	—	—	—	—	—	
3·85	·5	1·0404	15	152·0	18	—	—	304	—	—	—	—	—	—	
·00459	·00057	—	—	—	18	—	950[7]	1010	—	—	—	—	—	—	
·00604	·00075	—	—	—	18	—	910	967	—	—	—	—	—	—	
·0104	·00129	—	—	—	18	—	850	903	—	—	—	—	—	—	
·0270	·00335	—	—	—	18	—	760	808	—	—	—	—	—	—	
7·18	·961	1·0780	15	228·0[8]	18	—	—	252	—	—	—	—	—	—	
9·34	1·276	1·1012	15	274·0	18	—	—	228	—	—	—	—	—	—	
11·88	1·668	1·1317	15	319·0	18	—	—	203	—	—	—	—	—	—	
15·60	2·282	1·1790	15	378·0	18	—	—	176	—	—	—	—	—	—	
17·75	2·656	1·2063	15	425·0	18	—	—	170	—	—	—	—	—	—	
19·61	2·996	1·2310	15	430·0	18	—	—	153	—	—	—	—	—	—	
20·41	3·148	1·2430	15	431·0	18	—	—	146	—	—	—	—	—	—	
22·44	3·539	1·2710	15	440·0	18	—	—	132	—	—	—	—	—	—	
22·59	3·574	1·2746	15	440·0	18	—	—	131	—	—	—	—	—	—	
23·15	3·603	1·2832	15	441·0	18	—	—	130	—	—	—	—	—	—	
23·66	3·788	1·2901	15	445·0	18	—	—	125	—	—	—	—	—	—	
24·88	3·913	1·2986	15	442·0	18	—	—	120	—	—	—	—	—	—	
25·28	4·116	1·3120	15	439·0	18	—	—	113	—	—	—	—	—	—	
26·81	4·448	1·3370	15	431·0	18	—	—	103	—	—	—	—	—	—	
32·50	5·752	1·4260	15	374·0	18	—	—	69	—	—	—	—	—	—	
33·71	—	—	—	359·0	18	—	—	—	—	—	—	—	—	—	
35·04	—	—	—	336·0	18	—	—	—	—	—	—	—	—	—	
37·81	—	—	—	294·0	18	—	—	—	—	—	—	—	—	—	

Copper Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}CuSO_4$, 79·78.

·00008	·00001	—	—	—	18	—	1086[1]	1154	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·00016	·00002	—	—	—	18	—	1084	1152	—	—	—	—	—	—	
·00048	·00006	—	—	—	18	—	1074	1142	—	—	—	—	—	—	
·0008	·0001	—	—	—	18	—	1062	1129	—	—	—	—	—	—	
·0016	·0002	—	—	—	18	—	1039	1104	—	—	1·0	675[4]	17·6	—	[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0048	·0006	—	—	—	18	—	987	1049	—	—	—	—	—	—	
·008	·001	—	—	—	18	—	950	1009	—	—	·0625	1073[5]	25·0	—	
·016	·002	—	—	—	18	—	873	928	—	—	·125	1052	25·0	—	
·048	·006	—	—	—	18	—	740	787	—	—	·25	1012	25·0	—	[3] Hittorf, *Pogg. Annal.* vol. xcviii. p. 196.
·08	·01	—	—	—	18	·0229	675	717	—	—	·5	942	25·0	—	
·239	·03	1·0015	18·0	—	18	—	537	571	—	—	1·0	805	25·0	—	
·397	·05	1·0034	18·0	—	18	—	479	509	—	—	—	—	—	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·671	·0846	1·0071	4·4	—	—	—	—	—	·638[2]	4·4	—	—	—	—	
·791	·1	1·0078	18·0	—	18	—	424	451	—	—	—	—	—	—	
1·282	·163	1·0135	4·8	—	—	—	—	—	·651	4·3	—	—	—	—	
2·457	·315	1·0254	3·0	—	—	—	—	—	·644	4·5	—	—	—	—	
3·847	·5	1·0380	18·0	—	18	·0216	288	306	—	—	—	—	—	—	[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 88.
5·235	·692	1·0553	3·6	—	—	—	—	—	·675	5·5	—	—	—	—	
7·418	1·0	1·0758	18·0	—	18	·0218	241	256	—	—	—	—	—	—	
9·47	1·31	1·1036	4·9	—	—	—	—	—	·712	6·5	—	—	—	—	
13·6	1·962	1·1521	4·5	—	—	—	—	—	·724	5·5	—	—	—	—	
—	3·0	—	—	—	18	·0241	150	159	—	—	—	—	—	—	
·00486	·00061	—	—	—	18	—	1020[2]	1084	—	—	—	—	—	—	
·00622	·00078	—	—	—	18	—	970	1031	—	—	—	—	—	—	
·00989	·00124	—	—	—	18	—	950	1010	—	—	—	—	—	—	
·0156	·00196	—	—	—	18	—	840	893	—	—	—	—	—	—	
·0251	·00315	—	—	—	18	—	800	850	—	—	—	—	—	—	
·0411	·0064	—	—	—	18	—	700	744	—	—	—	—	—	—	

Cadmium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}CdSO_4$, 104·03.

·0289	·00278	·99893	18	2·3[1]	18	·0230	827	879	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 494.
·0489	·00482	·99915	18	3·62	18	·0230	750	797	—	—	—	—	—	—	

Cadmium Sulphate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}CdSO_4$, 104·03.

·0999	·00961	·99961	18°	6·43	18°	·0222	668	710	—	—	·125	1057[4]	25°	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 193.
—	—	—	—	—	—	—	—	—	—	—	·25	1014	25	—	
·495	·0479	1·0034	18	22·24	18	·0211	459	499	—	—	·5	944	25	—	
·981	·0954	1·0084	18	37·82	18	·0207	396	421	—	—	1·0	811	25	—	
·282	·0272	1·0015	18	14·3[2]	18	·0221	525	558	—	—	—	—	—	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
1·011	·0983	1·0085	18	38·9	18	·0210	396	421	—	—	—	—	—	—	
5·08	·514	1·0495	18	137·0	18	·0206	266	283	—	—	—	—	—	—	
10·11	1·076	1·1039	18	232·0	18	·0206	216	230	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
25·03	3·127	1·2955	18	400·0	18	·0223	128	136	—	—	—	—	—	—	
36·07	5·133	1·4756	18	392·0	18	·0255	76	81	—	—	—	—	—	—	
·00655	·00063	—	—	—	18	—	930[3]	989	—	—	—	—	—	—	
·00936	·0009	—	—	—	18	—	890	946	—	—	—	—	—	—	
·01633	·00157	—	—	—	18	—	820	871	—	—	—	—	—	—	

Ferrous Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}FeSO_4$, 76·03.

·00684	·0009	—	—	—	18	·0296	780[1]	829	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00973	·00128	—	—	—	18	·0230	760	808	—	—	—	—	—	—	
·01193	·00157	—	—	—	18	·0270	730	776	—	—	—	—	—	—	
·02417	·00318	—	—	—	18	—	670	712	—	—	—	—	—	—	

Nickel Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}NiSO_4$, 77·33.

—	—	—	—	—	—	—	—	—	—	—	·125	1059[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00572	·00074	—	—	—	18	—	730[1]	776	—	—	·25	1016	25	—	
·00727	·00094	—	—	—	18	—	720	765	—	—	·5	941	25	—	
·01392	·0018	—	—	—	18	—	680	723	—	—	1·0	803	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 80.

Cobalt Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}CoSO_4$, 77·53.

—	—	—	—	—	—	—	—	—	—	—	·125	1050[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00729	·00094	—	—	—	18	—	810[1]	861	—	—	·25	1015	25	—	
·01046	·00135	—	—	—	18	—	780	829	—	—	·5	942	25	—	
·02054	·00265	—	—	—	18	—	700	744	—	—	1·0	807	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.

Aluminium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{6}Al_2(SO_4)_3$, 41·02.

·00266	·00065	—	—	—	18	—	810[1]	861	—	—	·125	1053[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00640	·00156	—	—	—	18	—	700	744	—	—	·25	1010	25	—	
·00865	·00211	—	—	—	18	—	660	701	—	—	·5	927	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	777	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.

Methyl Sulphuric Acid.

Equivalent Gramme Molecule, HCH_3SO_4, 112·07.

·0109	·000976	—	—	368·1[1]	25	—	—	3913[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·0218	·00195	—	—	365·2	25	—	—	3882	—	—	—	—	—	—	
·0435	·0039	—	—	362·8	25	—	—	3857	—	—	—	—	—	—	
·087	·0078	—	—	357·8	25	—	—	3803	—	—	—	—	—	—	
·174	·0156	—	—	351·4	25	—	—	3735	—	—	—	—	—	—	[2] At 25°.
·349	·0312	—	—	345·0	25	—	—	3667	—	—	—	—	—	—	

Sodium Methyl Sulphate.

Equivalent Gramme Molecule, $NaCH_3SO_4$, 134·1.

·0130	·000976	—	—	91·4[1]	25	—	—	972[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0261	·00195	—	—	89·2	25	—	—	948	—	—	—	—	—	—	
·0522	·0039	—	—	86·9	25	—	—	924	—	—	—	—	—	—	
·1045	·0078	—	—	84·8	25	—	—	901	—	—	—	—	—	—	
·209	·0156	—	—	82·2	25	—	—	874	—	—	—	—	—	—	[2] At 25°.
·418	·0312	—	—	79·6	25	—	—	846	—	—	—	—	—	—	

Ethyl Sulphuric Acid.

Equivalent Gramme Molecule, $HC_2H_5SO_4$, 126·07.

			°		°				°				°		
·0122	·000976	—	—	367·4[1]	25	—	—	395[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·0245	·00195	—	—	363·9	25	—	—	3868	—	—	—	—	—	—	
·049	·0039	—	—	359·3	25	—	—	3819	—	—	—	—	—	—	
·098	·0078	—	—	353·4	25	—	—	3757	—	—	—	—	—	—	[2] At 25°.
·196	·0156	—	—	347·6	25	—	—	3695	—	—	—	—	—	—	
·392	·0312	—	—	340·9	25	—	—	3624	—	—	—	—	—	—	

Sodium Ethyl Sulphate.

Equivalent Gramme Molecule, $NaC_2H_5SO_4$, 148·1.

·0144	·000976	—	—	87·5[1]	25	—	—	930[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0289	·00195	—	—	85·3	25	—	—	907	—	—	—	—	—	—	
·0578	·0039	—	—	83·4	25	—	—	886	—	—	—	—	—	—	
·1155	·0078	—	—	82·1	25	—	—	873	—	—	—	—	—	—	[2] At 25°.
·231	·0156	—	—	79·8	25	—	—	848	—	—	—	—	—	—	
·462	·0312	—	—	77·2	25	—	—	821	—	—	—	—	—	—	

Sulphurous Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SO_3$, 41·03.

·002	·000498	—	—	83·6[1]	25	—	—	1888[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 314.
·004	·000976	—	—	80·4	25	—	—	1815	—	—	—	—	—	—	
·008	·00195	—	—	77·1	25	—	—	1741	—	—	—	—	—	—	
·016	·0039	—	—	72·5	25	—	—	1637	—	—	—	—	—	—	
·032	·0078	—	—	66·5	25	—	—	1501	—	—	—	—	—	—	[2] At 25°.
·064	·0156	—	—	58·9	25	—	—	1330	—	—	—	—	—	—	
·128	·0312	—	—	50·1	25	—	—	1132	—	—	—	—	—	—	
·256	·0625	—	—	41·6	25	—	—	939	—	—	—	—	—	—	
·512	·125	—	—	32·8	25	—	—	741	—	—	—	—	—	—	
—	·25	—	—	25·4	25	—	—	574	—	—	—	—	—	—	
—	·5	—	—	19·2	25	—	—	434	—	—	—	—	—	—	

Selenic Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SeO_4$, 72·4.

·00176	·000244	—	—	173·4[1]	25	—	—	3915[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 818.
·00352	·000488	—	—	174·4	25	—	—	3937	—	—	—	—	—	—	
·00705	·000976	—	—	173·4	25	—	—	3915	—	—	—	—	—	—	
·0141	·00195	—	—	169·7	25	—	—	3832	—	—	—	—	—	—	[2] At 25°.

·0282	·0039	—	—	164·4	25	—	—	3712	—	—	—	—	—	—	
·0565	·0078	—	—	157·9	25	—	—	3565	—	—	—	—	—	—	
·113	·0156	—	—	148·7	25	—	—	3357	—	—	—	—	—	—	
·226	·0312	—	—	138·3	25	—	—	3122	—	—	—	—	—	—	
·452	·0625	—	—	127·0	25	—	—	2867	—	—	—	—	—	—	
—	·125	—	—	117·7	25	—	—	2658	—	—	—	—	—	—	
—	·25	—	—	109·9	25	—	—	2481	—	—	—	—	—	—	
—	·5	—	—	103·2	25	—	—	2330	—	—	—	—	—	—	
—	1·	—	—	97·3	25	—	—	2197	—	—	—	—	—	—	

Sodium Selenate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2SeO_4$, 94·44.

·0092	·000976	—	—	115·2[1]	25	—	—	1225[2]	—	—	—	—	—	—	
·0184	·00195	—	—	111·6	25	—	—	1186	—	—	—	—	—	—	
·0368	·0039	—	—	107·4	25	—	—	1126	—	—	—	—	—	—	
·0735	·0078	—	—	103·4	25	—	—	1099	—	—	—	—	—	—	
·147	·0156	—	—	98·1	25	—	—	1043	—	—	—	—	—	—	
·294	·0312	—	—	92·7	25	—	—	986	—	—	—	—	—	—	

[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 106.

[2] At 25°.

Phosphoric Acid.

Equivalent Gramme Molecule, $\frac{1}{3}H_3PO_4$, 32·67.

·0012	·000368	—	—	78·8[1]	25	—	—	1186	—	—	—	—	—	—	
·0024	·000735	—	—	79·8	25	—	—	1201	—	—	—	—	—	—	
·0048	·00147	—	—	79·0	25	—	—	1189	—	—	—	—	—	—	
·0096	·00295	—	—	75·4	25	—	—	1135	—	—	—	—	—	—	
·0192	·0059	—	—	69·9	25	—	—	1052	—	—	—	—	—	—	
·0385	·0118	—	—	61·8	25	—	—	931	—	—	—	—	—	—	
·077	·0235	—	—	53·1	25	—	—	799	—	—	—	—	—	—	
·154	·047	—	—	43·0	25	—	—	647	—	—	—	—	—	—	
·307	·094	—	—	34·4	25	—	—	518	—	—	—	—	—	—	
·598	·188	1·0029	15	27·1	25	—	—	408	—	—	·375	1057[2]	25	—	
1·215	·375	1·0076	15	21·3	25	—	—	321	—	—	·75	1026	25	—	
2·41	·75	1·0136	15	17·0	25	—	—	256	—	—	1·5	964	25	—	
4·76	1·5	1·0263	15	14·2	25	—	—	214	—	—	3·	849	25	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 460.

[2] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.

Potassium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CO_3$, 69·13.

·000069	·00001	—	°	—	18	—	865[1]	919	—	°	—	—	°	—	—
·000138	·00002	—	—	—	18	—	882	938	—	—	—	—	—	—	—
·000415	·00006	—	—	—	18	—	917	975	—	—	—	—	—	—	—
·000691	·0001	—	—	—	18	—	995	1058	—	—	—	—	—	—	—
·00138	·0002	—	—	—	18	—	1128	1199	—	—	—	—	—	—	—
·00415	·0006	—	—	—	18	—	1222	1299	—	—	—	—	—	—	—
·00691	·001	—	—	—	18	—	1221	1298	—	—	—	—	—	—	—
·0138	·002	—	—	—	18	—	1199	1274	—	—	—	—	—	—	—
·0415	·006	—	—	—	18	—	1124	1195	—	—	—	—	—	—	—
·0691	·01	—	—	—	18	·0249	1083	1151	—	—	—	—	—	—	—
—	·029	—	—	—	—	—	—	—	·302[2]	—	—	—	—	—	—
·207	·03	—	—	—	18	—	989	1051	—	—	—	—	—	—	—
·344	·05	1·0026	15	—	18	—	942	1001	—	—	—	—	—	—	—
—	·074	—	—	—	—	—	—	—	·372	—	—	—	—	—	—
·687	·1	1·0060	15	—	18	—	879	934	—	—	—	—	—	—	—
—	·151	—	—	—	—	—	—	—	·377	—	—	—	—	—	—
—	·441	—	—	—	—	—	—	—	·434	—	—	—	—	—	—
3·354	·5	1·0306	15	—	18	·0227	728	774	—	—	—	—	—	—	—
—	·764	—	—	—	—	—	—	—	·437	—	—	—	—	—	—
6·522	1·	1·0600	15	—	18	·0219	660	702	·4	—	1·	809[3]	17·6	—	—
—	1·607	—	—	—	—	—	—	—	·416	—	—	—	—	—	—
12·39	2·	1·1162	15	—	18	·0211	584	620	—	—	—	—	—	—	—
—	3·	—	—	—	18	·0210	517	550	—	—	—	—	—	—	—
—	3·147	—	—	—	—	—	—	—	·404	—	—	—	—	—	—
27·21	5·	1·2702	15	—	18	·0216	403	428	—	—	—	—	—	—	—
—	8·112	—	—	—	—	—	—	—	·341	—	—	—	—	—	—
46·14	10·	1·4959	15	—	18	·0285	169	180	—	—	—	—	—	—	—
·407	·059	1·0032	15	52[4]	18	—	874	929	—	—	—	—	—	—	—
·810	·118	1·0073	15	97	18	—	820	874	—	—	—	—	—	—	—
1·608	·236	1·0147	15	181	18	—	767	815	—	—	—	—	—	—	—
3·171	·472	1·0289	15	334	18	—	707	751	—	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.

[2] Kuschel, *Wied. Annal.* vol. xiii. p. 289.

[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[4] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.

Lithium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}Li_2CO_3$, 37·02.

·00648	·00175	—	—	—	—	—	830[1]	882	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0111	·0030	—	—	—	—	—	790	840	—	—	—	—	—	—	
·0148	·0040	—	—	—	—	—	780	829	—	—	—	—	—	—	
·503	·136	—	—	—	—	—	—	—	·593[2]	—	—	—	—	—	[2] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·232	—	—	—	—	—	—	—	·582	—	—	—	—	—	

Sodium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2CO_3$, 53·04.

·000053	·00001	—	—	—	18	—	697[1]	740	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000106	·00002	—	—	—	18	—	715	760	—	—	—	—	—	—	
·000318	·00006	—	—	—	18	—	790	840	—	—	—	—	—	—	
·00053	·0001	—	—	—	18	—	874	929	—	—	—	—	—	—	
·00106	·0002	—	—	—	18	—	988	1050	—	—	—	—	—	—	
·00318	·0006	—	—	—	18	—	1046	1112	—	—	—	—	—	—	
·0053	·001	—	—	—	18	—	1037	1102	—	—	—	—	—	—	
·0106	·002	—	—	—	18	—	1010	1073	—	—	—	—	—	—	
·0318	·006	—	—	—	18	—	956	1016	—	—	—	—	—	—	
·053	·01	—	—	—	18	·0265	899	955	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·159	·03	—	—	—	18	—	799	850	—	—	—	—	—	—	
·264	·05	1·0019	15	—	18	—	751[1]	798	—	—	—	—	—	—	
·5	·093	—	—	—	—	—	—	—	·474[2]	—	—	—	—	—	
·528	·1	1·0046	15	—	18	—	682	725	—	—	—	—	—	—	
—	·189	—	—	—	—	—	—	—	·519	—	—	—	—	—	
2·592	·5	1·0271	15	—	18	·0244	510	542	—	—	—	—	—	—	
5·0	·985	—	—	—	—	—	—	—	·548	—	—	—	—	—	
5·038	1·	1·0529	15	—	18	·0252	427	454	—	—	—	—	—	—	
—	2·844	—	—	—	—	—	—	—	·530	—	—	—	—	—	
13·86	3·	1·1479	15	—	18	·0289	254	270	—	—	—	—	—	—	[3] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
·659	·125	1·0060	15	79[3]	18	—	632	672	—	—	—	—	—	—	
1·307	·25	1·0137	15	142	18	—	568	603	—	—	—	—	—	—	
2·592	·5	1·0271	15	248	18	—	496	527	—	—	—	—	—	—	
5·038	1·	1·0529	15	433	18	—	433	460	—	—	—	—	—	—	

Potassium Chromate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CrO_4$, 97·33.

			°		°					°			°		
·638	·066	1·0044	19·5	60·1[1]	18	—	910	967	—	—	1·349[3]	882	20	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
1·270	·132	1·0101	19·5	113·0	18	—	856	909	—	—	2·363	802	20	—	
2·515	·264	1·0203	19·5	212·0	18	—	803	853	—	—	4·407	620	20	—	
4·932	·528	1·0402	19·5	396·0	18	—	750	797	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 371.
9·50	—	—	—	—	—	—	—	—	·512[2]	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 1.

Ammonium Chromate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2CrO_4$, 76·24.

—	·0634	—	—	52[1]	18	—	820	871	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·1268	—	—	97	18	—	765	813	—	—	—	—	—	—	
—	·2536	—	—	177	18	—	698	742	—	—	—	—	—	—	
—	·517	—	—	318	18	—	615	653	—	—	—	—	—	—	

Potassium Bichromate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2Cr_2O_7$, 147·52.

1·033	·0706	1·0073	19·5	62[1]	18	—	878	933	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
2·050	·1413	1·0153	19·5	117	18	—	829	880	—	—	—	—	—	—	
4·040	·2826	1·0303	19·5	208	18	—	736	782	—	—	—	—	—	—	
6·390	—	—	—	—	—	—	—	—	·502[2]	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 371.
7·891	·5652	1·0553	19·5	415	18	—	734	780	—	—	—	—	—	—	

Ammonium Bichromate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2Cr_2O_7$, 126·44.

—	·0883	—	—	72·7[1]	18	—	823	874	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·1767	—	—	133·0	18	—	752	799	—	—	—	—	—	—	
—	·3534	—	—	252·0	18	—	713	757	—	—	—	—	—	—	
—	·7068	—	—	472·0	18	—	667	708	—	—	—	—	—	—	

Hydrocyanic Acid.

Equivalent Gramme Molecule, HCN, 26·98.

·084	·0312	—	—	·108[1]	25	—	—	4·88[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 304.
·168	·0625	—	—	·101	25	—	—	4·56	—	—	—	—	—	—	
·337	·125	—	—	·090	25	—	—	4·06	—	—	—	—	—	—	
·675	·25	—	—	·077	25	—	—	3·48	—	—	—	—	—	—	[2] At 25°.

Potassium Cyanide.

Equivalent Gramme Molecule, KCN, 65·02.

·946	—	—	—	—	—	—	—	—	·47[2]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
3·20	·5	1·0154	15	488[1]	18	·0208	976	1037	—	—	—	—	—	—	
6·30	1·	1·0312	15	938	18	·0195	938	997	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi.
11·55	—	—	—	—	—	—	—	—	·457	—	—	—	—	—	

Sulphocyanic Acid.

Equivalent Gramme Molecule, HCNS, 58·96.

·00145	·000244	—	—	84·1[1]	25	—	—	3797[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 305.
·0029	·000488	—	—	85·8	25	—	—	3874	—	—	—	—	—	—	
·0058	·000976	—	—	86·3	25	—	—	3897	—	—	—	—	—	—	
·0115	·00195	—	—	86·8	25	—	—	3919	—	—	—	—	—	—	[2] At 25°.
·023	·0039	—	—	86·5	25	—	—	3905	—	—	—	—	—	—	
·046	·0078	—	—	86·5	25	—	—	3905	—	—	—	—	—	—	
·092	·0156	—	—	85·2	25	—	—	3847	—	—	—	—	—	—	
·184	·0312	—	—	84·2	25	—	—	3802	—	—	—	—	—	—	
—	·0625	—	—	82·8	25	—	—	3739	—	—	—	—	—	—	
—	·125	—	—	81·2	25	—	—	3666	—	—	—	—	—	—	
—	·25	—	—	79·3	25	—	—	3581	—	—	—	—	—	—	
—	·5	—	—	76·7	25	—	—	3463	—	—	—	—	—	—	

Hydroferrocyanic Acid.

Equivalent Gramme Molecule, $\frac{1}{4}H_4FeCy_6$, 53·95.

·00131	·000244	—	—	80·4[1]	25	—	—	3630[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 307.
·00262	·000488	—	—	76·2	25	—	—	3440	—	—	—	—	—	—	
·00525	·000976	—	—	72·0	25	—	—	3251	—	—	—	—	—	—	
·0105	·00195	—	—	67·1	25	—	—	3030	—	—	—	—	—	—	[2] At 25°.
·0210	·0039	—	—	62·7	25	—	—	2831	—	—	—	—	—	—	
·0421	·0078	—	—	58·6	25	—	—	2646	—	—	—	—	—	—	
·0841	·0156	—	—	55·1	25	—	—	2488	—	—	—	—	—	—	

Formic Acid.

Equivalent Gramme Molecule, HCOOH, 46.

·00225	·000488	—	—	36·00[1]	25	—	—	1622[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 445.
·0045	·000976	—	—	29·04	25	—	—	1311	—	—	—	—	—	—	
·0090	·00195	—	—	22·54	25	—	—	1018	—	—	—	—	—	—	
·0180	·0039	—	—	17·00	25	—	—	768	—	—	—	—	—	—	[2] At 25°.
·0359	·0078	—	—	12·58	25	—	—	568	—	—	—	—	—	—	
·0718	·0156	—	—	9·18	25	—	—	414	—	—	—	—	—	—	
·1435	·0312	—	—	6·63	25	—	—	299	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·287	·0625	—	—	4·79	25	—	—	217	—	—	·125[3]	1087	25	—	
·574	·125	1·0015	25	3·43	25	—	—	155	—	—	·25	1083	25	—	
—	·25	1·0030	25	2·46	25	—	—	111	—	—	·5	1075	25	—	
—	·5	1·0058	25	1·76	25	—	—	79	—	—	1·0	1060	25	—	[4] Berthelot, *Annales de Chimie*, series 6, vol. xxiii. p. 89.
·0046	·001	—	—	103[4]	17	—	—	1405	—	—	—	—	—	—	
·0092	·002	—	—	77·8	17	—	—	1061	—	—	—	—	—	—	
·046	·01	—	—	38·4	17	·018	—	524	—	—	—	—	—	—	
·115	·025	—	—	24·9	17	—	—	340	—	—	—	—	—	—	
·23	·05	—	—	17·9	17	—	—	245	—	—	—	—	—	—	
·46	·1	—	—	12·9	17	—	—	176	—	—	—	—	—	—	

Potassium Formate.

Equivalent Gramme Molecule, HCOOK, 84·13.

·0082	·000976	—	—	120·1[1]	25	—	—	1277[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0164	·00195	—	—	117·3	25	—	—	1247	—	—	—	—	—	—	
·0328	·0039	—	—	114·7	25	—	—	1219	—	—	—	—	—	—	
·0655	·0078	—	—	112·3	25	—	—	1194	—	—	—	—	—	—	
·131	·0156	—	—	108·8	25	—	—	1156	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 40.
·262	·0312	—	—	105·8	25	—	—	1124	—	—	—	—	—	—	
·0042	·0005	—	—	95[2]	17	—	—	1341	—	—	—	—	—	—	[3] At 25°.
·0168	·002	—	—	91·5	17	—	—	1291	—	—	—	—	—	—	
·042	·005	—	—	87·6	17	·023	—	1236	—	—	—	—	—	—	

Sodium Formate.

Equivalent Gramme Molecule, HCOONa, 68·04.

·0066	·000976	—	—	98·9[1]	25	—	—	1051[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0132	·00195	—	—	96·9	25	—	—	1030	—	—	—	—	—	—	
·0265	·0039	—	—	94·7	25	—	—	1007	—	—	·125[3]	1068	25	—	

·053	·0078	—	—	92·0	25	—	—	978	—	—	·25	1046	25	—	[2] At 25°.
·106	·0156	—	—	89·0	25	—	—	946	—	—	·5	998	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·212	·0312	—	—	85·8	25	—	—	912	—	—	1·0	906	25	—	

Lithium Formate.

Equivalent Gramme Molecule, HCOOLi, 52·02.

·00505	·000976	—	—	88·1[1]	25	—	—	936[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·0101	·00195	—	—	85·8	25	—	—	912	—	—	—	—	—	—	
·0202	·0039	—	—	83·4	25	—	—	886	—	—	—	—	—	—	
·0405	·0078	—	—	80·8	25	—	—	859	—	—	—	—	—	—	
·081	·0156	—	—	77·9	25	—	—	828	—	—	—	—	—	—	[2] At 25°.
·162	·0312	—	—	75·0	25	—	—	797	—	—	—	—	—	—	

Acetic Acid.

Equivalent Gramme Molecule, CH_3COOH, 60.

·00146	·000244	—	—	19·37[1]	25	—	—	785	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 444.
·00292	·000488	—	—	14·48	25	—	—	586	—	—	—	—	—	—	
·00585	·000976	—	—	10·48	25	—	—	424	—	—	—	—	—	—	
·0117	·00195	—	—	7·77	25	—	—	314	—	—	—	—	—	—	
·0234	·0039	—	—	5·66	25	—	—	229	—	—	—	—	—	—	[2] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·0468	·0078	—	—	4·08	25	—	—	166	—	—	—	—	—	—	
·0935	·0156	—	—	2·94	25	—	—	119	—	—	—	—	—	—	
·187	·0312	—	—	2·123	25	—	—	86·1	—	—	—	—	—	—	
·374	·0625	—	—	1·514	25	—	—	61·4	—	—	—	—	—	—	[3] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 197.
·748	·125	1·0003	15	1·078	25	—	—	43·7	—	—	·125	1074[2]	25	—	
1·494	·25	1·0014	15	·756	25	—	—	30·6	—	—	·25	1060	25	—	
2·982	·5	1·0036	15	·520	25	—	—	21·1	—	—	·5	1031	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	982	25	—	
·00006	·00001	—	—	—	18	—	1304[3]	1386	—	—	—	—	—	—	
·00012	·00002	—	—	—	18	—	1328	1412	—	—	—	—	—	—	
·00036	·00006	—	—	—	18	—	1133	1204	—	—	—	—	—	—	
·0006	·0001	—	—	—	18	—	995	1058	—	—	—	—	—	—	
·0012	·0002	—	—	—	18	—	796	846	—	—	—	—	—	—	
·0036	·0006	—	—	—	18	—	470	500	—	—	—	—	—	—	
·006	·001	—	—	—	18	—	380	404	—	—	—	—	—	—	
·012	·002	—	—	—	18	—	283	301	—	—	—	—	—	—	
·036	·006	—	—	—	18	—	170	181	—	—	—	—	—	—	
·06	·01	—	—	—	18	—	132	140	—	—	—	—	—	—	

Acetic Acid—*continued.*

Equivalent Gramme Molecule, CH_3COOH, 60.

			°		°					°			°	
·18	·03	—	—	—	18	—	79	84	—	—	—	—	—	—
·30	·05	—	—	—	18	—	62	66	—	—	—	—	—	—
·60	·1	1·0002	15	—	18	—	43	46	—	—	—	—	—	—
2·98	·5	1·0036	15	—	18	—	19	20·2	—	—	—	—	—	—
5·95	1·	1·0080	15	—	18	—	12	12·7	—	—	—	—	—	—
17·56	3·	1·0246	15	—	18	—	5·2	5·5	—	—	—	—	—	—
28·87	5·	1·0389	15	—	18	—	2·6	2·8	—	—	—	—	—	—
56·39	10·	1·0644	15	—	18	—	·5	·53	—	—	—	—	—	—
·006	·001	—	—	35·0[4]	17	—	—	425	—	—	—	—	—	—
·012	·002	—	—	25·2	17	—	—	306	—	—	—	—	—	—
·030	·005	—	—	16·2	17	—	—	196	—	—	—	—	—	—
·060	·01	—	—	11·6	17	·018	—	141	—	—	—	—	—	—

[4] Berthelot, *Annales de Chimie*, vol. xxiii. p. 43.

Potassium Acetate.

Equivalent Gramme Molecule, CH_3COOK, 98·13.

·000098	·00001	—	—	—	18	—	939[1]	998	—	—	—	—	—	—
·000196	·00002	—	—	—	18	—	943	1002	—	—	—	—	—	—
·000588	·00006	—	—	—	18	—	935	994	—	—	—	—	—	—
·00098	·0001	—	—	—	18	—	934	993	—	—	—	—	—	—
·00196	·0002	—	—	—	18	—	933	992	—	—	—	—	—	—
·00588	·0006	—	—	—	18	—	923	981	—	—	—	—	—	—
·0098	·001	—	—	—	18	—	919	977	—	—	—	—	—	—
·0196	·002	—	—	—	18	—	913	970	—	—	—	—	—	—
·0588	·006	—	—	—	18	—	891	947	—	—	—	—	—	—
·098	·01	—	—	—	18	·0229	879	934	—	—	—	—	—	—
·294	·03	—	—	—	18	—	841	894	—	—	1·	735[3]	17·6	—
—	·05	—	—	—	18	—	820	872	—	—	—	—	—	—
—	·1	—	—	—	18	—	784	833	—	—	—	—	—	—
1·057	·114	1·0051	14	—	—	—	—	—	·324[2]	—	—	—	—	—
—	·5	—	—	—	18	·0224	671	713	—	—	—	—	—	—
9·37	1·	1·0467	18·6	—	18	·0220	594	631	—	—	—	—	—	—
—	3·	—	—	—	18	·0227	381	405	—	—	—	—	—	—
—	5·	—	—	—	18	·0252	240	255	—	—	—	—	—	—
42·7	5·4	1·2396	11	—	—	—	—	—	·325	—	—	—	—	—
—	10·	—	—	—	18	·0421	30	32	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.

[2] Hittorf, *Pogg. Annal.* vol. cii. p. 42.

[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

·0095	·000976	—	—	105·1[4]	25	—	—	943	—	—	—	—	—	—	[4] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0191	·00195	—	—	103·1	25	—	—	934	—	—	—	—	—	—	
·0382	·0039	—	—	100·4	25	—	—	915	—	—	—	—	—	—	
·0765	·0078	—	—	98·2	25	—	—	900	—	—	—	—	—	—	
·153	·0156	—	—	95·4	25	—	—	874	—	—	—	—	—	—	[5] Berthelot, *Annales de Chimie*, vol. xxiii. p. 43.
·306	·0312	—	—	92·9	25	—	—	851	—	—	—	—	—	—	
·0049	·0005	—	—	83·6[5]	17	—	—	1019	—	—	—	—	—	—	
·0196	·002	—	—	80·5	17	—	—	982	—	—	—	—	—	—	
·0294	·0033	—	—	78·0	17	—	—	951	—	—	—	—	—	—	
·049	·005	—	—	77·2	17	—	—	942	—	—	—	—	—	—	
·059	·0066	—	—	76·5	17	—	—	933	—	—	—	—	—	—	
·098	·01	—	—	75·4	17	—	—	920	—	—	—	—	—	—	

Sodium Acetate.

Equivalent Gramme Molecule, CH_3COONa, 82·04.

1·17	·142	1·0062	11	—	—	—	—	—	·443[3]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
2·36	·288	1·0125	5·5	—	—	—	—	—	·424	—	—	—	—	—	
—	·5	—	—	233[1]	18	·0253	466	495	—	—	—	—	—	—	
—	1·	—	—	389	18	·0255	389	413	—	—	·125	1047[4]	25	—	[2] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
12·22	1·6	1·0661	13	—	—	—	—	—	·421	—	·25	1003	25	—	
—	2·	—	—	561	18	·0275	280	297	—	—	·5	926	25	—	
—	3·	—	—	609	18	·0306	203	215	—	—	1·	785	25	—	
26·26	3·64	1·1455	7·7	—	—	—	—	—	·415	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 379.
—	4·	—	—	575	18	·0340	119	126	—	—	—	—	—	—	
—	5·	—	—	495	18	·0410	99	105	—	—	—	—	—	—	
·008	·000976	—	—	84·9[2]	25	—	—	768	—	—	—	—	—	—	[4] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·016	·00195	—	—	83·3	25	—	—	754	—	—	—	—	—	—	
·032	·0039	—	—	81·2	25	—	—	735	—	—	—	—	—	—	
·064	·0078	—	—	79·0	25	—	—	715	—	—	—	—	—	—	
·128	·0156	—	—	76·4	25	—	—	691	—	—	—	—	—	—	
·256	·0312	—	—	73·6	25	—	—	666	—	—	—	—	—	—	

Monochloracetic Acid.

Equivalent Gramme Molecule, $CH_2ClCOOH$, 94·46.

·0023	·000244	—	—	68·69[1]	25	—	—	3102[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 446.
·0046	·000488	—	—	63·48	25	—	—	2866	—	—	—	—	—	—	
·0092	·000976	—	—	55·64	25	—	—	2512	—	—	—	—	—	—	
·0184	·00195	—	—	46·75	25	—	—	2111	—	—	—	—	—	—	[2] At 25°.

Monochloracetic Acid—*continued.*

Equivalent Gramme Molecule, $CH_2ClCOOH$, 94·46.

			°		°					°				°		
·0368	·0039	—	—	37·81	25	—	—	1707	—	—	—	—	—	—	
·0735	·0078	—	—	29·61	25	—	—	1337	—	—	—	—	—	—	
·147	·0156	—	—	22·85	25	—	—	1032	—	—	—	—	—	—	
·294	·0312	—	—	17·29	25	—	—	781	—	—	—	—	—	—	
·588	·0625	—	—	12·86	25	—	—	578	—	—	—	—	—	—	
—	·125	—	—	9·53	25	—	—	430	—	—	—	—	—	—	
—	·25	—	—	6·98	25	—	—	316	—	—	—	—	—	—	
—	·5	—	—	4·99	25	—	—	179	—	—	—	—	—	—	

Dichloracetic Acid.

Equivalent Gramme Molecule, $CHCl_2COOH$, 128·92.

·00312	·000244	—	—	79·28[1]	25	—	—	3600[2]	—	—	—	—	—	—	
·00625	·000488	—	—	80·94	25	—	—	3651	—	—	—	—	—	—	
·0125	·000976	—	—	80·48	25	—	—	3636	—	—	—	—	—	—	
·025	·00195	—	—	79·70	25	—	—	3601	—	—	—	—	—	—	
·050	·0039	—	—	76·30	25	—	—	3442	—	—	—	—	—	—	
·100	·0078	—	—	72·52	25	—	—	3271	—	—	—	—	—	—	
·200	·0156	—	—	67·56	25	—	—	3043	—	—	—	—	—	—	
·400	·0312	—	—	60·30	25	—	—	2720	—	—	—	—	—	—	
·800	·0625	—	—	52·08	25	—	—	2356	—	—	—	—	—	—	
—	·125	—	—	43·03	25	—	—	1912	—	—	—	—	—	—	
—	·25	—	—	34·42	25	—	—	1550	—	—	—	—	—	—	
—	·5	—	—	25·75	25	—	—	1161	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 446.

[2] At 25°.

Trichloracetic Acid.

Equivalent Gramme Molecule, $CCl_3CO{\cdot}OH$, 163·38.

·00398	·000244	—	—	77·84[1]	25	—	—	3515[2]	—	—	—	—	—	—	
·00795	·000488	—	—	79·10	25	—	—	3572	—	—	—	—	—	—	
·0159	·000976	—	—	79·68	25	—	—	3598	—	—	—	—	—	—	
·0318	·00195	—	—	79·58	25	—	—	3593	—	—	—	—	—	—	
·0635	·0039	—	—	79·12	25	—	—	3572	—	—	—	—	—	—	
·127	·0078	—	—	79·00	25	—	—	3567	—	—	—	—	—	—	
·254	·0156	—	—	78·55	25	—	—	3547	—	—	—	—	—	—	
·508	·0312	—	—	76·95	25	—	—	3475	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 822.

[2] At 25°.

—	·0625	—	—	74·62	25	—	—	3369	—	—	—	—	—	—	
—	·125	—	—	71·14	25	—	—	3212	—	—	—	—	—	—	
—	·25	—	—	65·63	25	—	—	2963	—	—	—	—	—	—	
—	·5	—	—	57·56	25	—	—	2599	—	—	—	—	—	—	

Monobromacetic Acid.

Equivalent Gramme Molecule, $CH_2BrCOOH$, 138·95.

·00338	·000244	—	—	69·97[1]	25	—	—	3159[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 822.
·00675	·000488	—	—	64·02	25	—	—	2891	—	—	—	—	—	—	
·0135	·000976	—	—	55·47	25	—	—	2505	—	—	—	—	—	—	
·027	·00195	—	—	46·14	25	—	—	2083	—	—	—	—	—	—	
·054	·0039	—	—	36·83	25	—	—	1663	—	—	—	—	—	—	[2] At 25°.
·108	·0078	—	—	28·52	25	—	—	1288	—	—	—	—	—	—	
·216	·0156	—	—	21·62	25	—	—	976	—	—	—	—	—	—	
·432	·0312	—	—	16·12	25	—	—	728	—	—	—	—	—	—	
·863	·0625	—	—	11·90	25	—	—	537	—	—	—	—	—	—	
—	·125	—	—	8·65	25	—	—	391	—	—	—	—	—	—	

Potassium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COOK, 201·51.

·0196	·000976	—	—	101·9[1]	25	—	—	1083[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·0392	·00195	—	—	99·5	25	—	—	1058	—	—	—	—	—	—	
·0785	·0039	—	—	96·8	25	—	—	1029	—	—	—	—	—	—	
·157	·0078	—	—	94·3	25	—	—	1002	—	—	—	—	—	—	
·314	·0156	—	—	91·7	25	—	—	975	—	—	—	—	—	—	[2] At 25°.
·628	·0312	—	—	88·5	25	—	—	941	—	—	—	—	—	—	

Sodium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COONa, 185·42.

·018	·000976	—	—	80·7[1]	25	—	—	856[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 100.
·036	·00195	—	—	78·7	25	—	—	837	—	—	—	—	—	—	
·072	·0039	—	—	76·8	25	—	—	816	—	—	—	—	—	—	
·144	·0078	—	—	74·8	25	—	—	795	—	—	—	—	—	—	
·288	·0156	—	—	72·6	25	—	—	772	—	—	—	—	—	—	[2] At 25°.
·576	·0312	—	—	70·0	25	—	—	744	—	—	—	—	—	—	

Lithium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COOLi, 169·4.

			°		°					°			°		
·0165	·000976	—	—	70·2[1]	25	—	—	746[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·033	·00195	—	—	68·1	25	—	—	724	—	—	—	—	—	—	
·066	·0039	—	—	66·0	25	—	—	702	—	—	—	—	—	—	
·132	·0078	—	—	64·2	25	—	—	682	—	—	—	—	—	—	
·264	·0156	—	—	62·0	25	—	—	659	—	—	—	—	—	—	[2] At 25°.
·528	·0312	—	—	59·9	25	—	—	637	—	—	—	—	—	—	

Propionic Acid.

Equivalent Gramme Molecule, C_2H_5COOH, 74.

·0018	·000244	—	—	18·2[1]	25	—	—	822[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 317.
·0036	·000448	—	—	13·19	25	—	—	596	—	—	—	—	—	—	
·0072	·000976	—	—	9·56	25	—	—	432	—	—	—	—	—	—	
·0144	·00195	—	—	6·88	25	—	—	310	—	—	—	—	—	—	
·0289	·0039	—	—	4·92	25	—	—	222	—	—	—	—	—	—	[2] At 25°.
·0578	·0078	—	—	3·50	25	—	—	158	—	—	—	—	—	—	
·1155	·0156	—	—	2·49	25	—	—	112	—	—	—	—	—	—	
·231	·0312	—	—	1·767	25	—	—	80	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·462	·0625	—	—	1·247	25	—	—	56	—	—	·125	1065[3]	25	—	
·924	·125	1·0011	25	·871	25	—	—	39	—	—	·25	1044	25	—	
1·846	·25	1·0019	25	·601	25	—	—	27	—	—	·5	994	25	—	
3·687	·5	1·0035	25	·403	25	—	—	18	—	—	1·	913	25	—	

Potassium Propionate.

Equivalent Gramme Molecule, C_2H_5COOK, 112·13.

·0110	·000976	—	—	103·0[1]	25	—	—	1095[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0219	·00195	—	—	101·1	25	—	—	1064	—	—	—	—	—	—	
·0438	·0039	—	—	97·4	25	—	—	1035	—	—	—	—	—	—	
·0875	·0078	—	—	94·9	25	—	—	1009	—	—	—	—	—	—	
·175	·0156	—	—	92·1	25	—	—	979	—	—	—	—	—	—	[2] At 25°.
·350	·0312	—	—	89·0	25	—	—	946	—	—	—	—	—	—	

Sodium Propionate.

Equivalent Gramme Molecule, C_2H_5COONa, 96·04.

·0094	·000976	—	—	80·4[1]	25	—	—	854[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0188	·00195	—	—	78·8	25	—	—	837	—	—	·125	1036[3]	25	—	[2] At 25°.
·0375	·0039	—	—	76·5	25	—	—	813	—	—	·25	983	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·075	·0078	—	—	74·5	25	—	—	792	—	—	·5	885	25	—	
·150	·0156	—	—	71·9	25	—	—	764	—	—	1·	711	25	—	
·300	·0312	—	—	69·4	25	—	—	737	—	—	—	—	—	—	

Lithium Propionate.

Equivalent Gramme Molecule, C_2H_5COOLi, 80·02.

·0078	·00976	—	—	69·5[1]	25	—	—	739[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·0156	·00195	—	—	67·5	25	—	—	717	—	—	—	—	—	—	
·0312	·0039	—	—	65·5	25	—	—	696	—	—	—	—	—	—	[2] At 25°.
·0625	·0078	—	—	63·5	25	—	—	675	—	—	—	—	—	—	
·125	·0156	—	—	60·6	25	—	—	644	—	—	—	—	—	—	
·250	·0312	—	—	57·9	25	—	—	615	—	—	—	—	—	—	

A. Brompropionic Acid.

Equivalent Gramme Molecule, $C_2H_4BrCOOH$, 152·95.

·00372	·000244	—	—	68·9[1]	—	—	—	3111[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 324.
·00745	·000488	—	—	62·2	—	—	—	2807	—	—	—	—	—	—	
·0149	·000976	—	—	53·7	—	—	—	2423	—	—	—	—	—	—	[2] At 25°.
·0298	·00195	—	—	44·7	—	—	—	2020	—	—	—	—	—	—	
·0595	·0039	—	—	36·1	—	—	—	1632	—	—	—	—	—	—	
·119	·0078	—	—	28·8	—	—	—	1299	—	—	—	—	—	—	
·238	·0156	—	—	22·6	—	—	—	1020	—	—	—	—	—	—	
·477	·0312	—	—	17·6	—	—	—	796	—	—	—	—	—	—	
—	·0625	—	—	13·7	—	—	—	619	—	—	—	—	—	—	
—	·125	—	—	10·5	—	—	—	475	—	—	—	—	—	—	
—	·25	—	—	7·9	—	—	—	355	—	—	—	—	—	—	
—	·5	—	—	5·6	—	—	—	252	—	—	—	—	—	—	

B. Iodopropionic Acid.

Equivalent Gramme Molecule, CH_2ICH_2COOH, 199·8.

			°		°					°			°		
·0049	·000244	—	—	36·0[1]	25	—	—	1628[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 825.
·0098	·000488	—	—	28·2	25	—	—	1272	—	—	—	—	—	—	
·0195	·000976	—	—	21·3	25	—	—	964	—	—	—	—	—	—	
·039	·00195	—	—	15·8	25	—	—	715	—	—	—	—	—	—	[2] At 25°.
·078	·0039	—	—	11·6	25	—	—	524	—	—	—	—	—	—	
·156	·0078	—	—	8·45	25	—	—	381	—	—	—	—	—	—	
·312	·0156	—	—	6·10	25	—	—	275	—	—	—	—	—	—	
·624	·0312	—	—	4·38	25	—	—	198	—	—	—	—	—	—	
—	·0625	—	—	3·12	25	—	—	141	—	—	—	—	—	—	
—	·125	—	—	2·22	25	—	—	100	—	—	—	—	—	—	
—	·25	—	—	1·53	25	—	—	69	—	—	—	—	—	—	

Butyric Acid.

Equivalent Gramme Molecule, C_3H_7COOH, 88.

·00214	·000244	—	—	18·0[1]	25	—	—	814[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 444.
·00428	·000488	—	—	13·4	25	—	—	604	—	—	—	—	—	—	
·00855	·000976	—	—	9·74	25	—	—	440	—	—	—	—	—	—	
·0171	·00195	—	—	7·01	25	—	—	317	—	—	—	—	—	—	[2] At 25°.
·0342	·0039	—	—	5·04	25	—	—	228	—	—	—	—	—	—	
·0685	·0078	—	—	3·59	25	—	—	162	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·137	·0156	—	—	2·56	25	—	—	116	—	—	—	—	—	—	
·274	·0312	—	—	1·81	25	—	—	82	—	—	—	—	—	—	
·548	·0625	—	—	1·27	25	—	—	58	—	—	·125	1060[3]	25	—	
1·099	·125	1·0006	25	·88	25	—	—	40	—	—	·25	1027	25	—	
2·197	·25	1·0013	25	·60	25	—	—	27	—	—	·5	966	25	—	
4·390	·5	1·0022	25	·39	25	—	—	18	—	—	1·	854	25	—	

Potassium Butyrate.

Equivalent Gramme Molecule, C_3H_7COOK, 126·13.

·0122	·000976	—	—	100·3[1]	25	—	—	1066[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0245	·00195	—	—	97·4	25	—	—	1035	—	—	—	—	—	—	
·049	·0039	—	—	94·8	25	—	—	1008	—	—	—	—	—	—	
·098	·0078	—	—	92·5	25	—	—	983	—	—	—	—	—	—	
·196	·0156	—	—	89·0	25	—	—	946	—	—	—	—	—	—	[2] At 25°.
·393	·0312	—	—	86·3	25	—	—	917	—	—	—	—	—	—	

Sodium Butyrate.

Equivalent Gramme Molecule, C_3H_7COONa, 110·04.

·0108	·000976	—	—	76·4[1]	25	—	—	812[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99. [2] At 25°. [3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·0215	·00195	—	—	75·0	25	—	—	797	—	—	·125	1025[3]	25	—	
·043	·0039	—	—	73·4	25	—	—	780	—	—	·25	962	25	—	
·086	·0078	—	—	71·2	25	—	—	757	—	—	·5	845	25	—	
·172	·0156	—	—	68·9	25	—	—	732	—	—	1·	652	25	—	
·343	·0312	—	—	66·2	25	—	—	703	—	—	—	—	—	—	

Lithium Butyrate.

Equivalent Gramme Molecule, C_3H_7COOLi, 94·02.

·0091	·000976	—	—	66·5[1]	25	—	—	707[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104. [2] At 25°.
·0182	·00195	—	—	64·7	25	—	—	688	—	—	—	—	—	—	
·0365	·0039	—	—	63·0	25	—	—	670	—	—	—	—	—	—	
·073	·0078	—	—	60·8	25	—	—	646	—	—	—	—	—	—	
·146	·0156	—	—	58·2	25	—	—	619	—	—	—	—	—	—	
·293	·0312	—	—	55·5	25	—	—	590	—	—	—	—	—	—	

Isobutyric Acid.

Equivalent Gramme Molecule, C_3H_7COOH, 88.

·00215	·000244	—	—	17·62[1]	25	—	—	797[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 318. [2] At 25°. [3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·0043	·000488	—	—	12·97	25	—	—	587	—	—	—	—	—	—	
·0086	·000976	—	—	9·50	25	—	—	430	—	—	—	—	—	—	
·0172	·00195	—	—	6·86	25	—	—	310	—	—	—	—	—	—	
·0345	·0039	—	—	4·95	25	—	—	224	—	—	—	—	—	—	
·069	·0078	—	—	3·55	25	—	—	161	—	—	—	—	—	—	
·138	·0156	—	—	2·54	25	—	—	115	—	—	—	—	—	—	
·275	·0312	—	—	1·81	25	—	—	82	—	—	—	—	—	—	
·550	·0625	—	—	1·27	25	—	—	57	—	—	·125[3]	1059	25	—	
1·100	·125	1·0004	25	·89	25	—	—	40	—	—	·25	1025	25	—	
2·198	·25	1·0008	25	·61	25	—	—	27·6	—	—	·5	968	25	—	
4·392	·5	1·0016	25	·39	25	—	—	17·6	—	—	1·	859	25	—	

Potassium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COOK, 126·13.

			°		°					°			°		
·0122	·000976	—	—	100·2[1]	25	—	—	1065[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0245	·00195	—	—	97·4	25	—	—	1035	—	—	—	—	—	—	
·049	·0039	—	—	94·9	25	—	—	1009	—	—	—	—	—	—	
·098	·0078	—	—	92·5	25	—	—	983	—	—	—	—	—	—	[2] At 25°.
·196	·0156	—	—	89·6	25	—	—	952	—	—	—	—	—	—	
·393	·0312	—	—	86·7	25	—	—	922	—	—	—	—	—	—	

Sodium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COONa, 110·04.

·0108	·000976	—	—	79·0[1]	25	—	—	840[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0215	·00195	—	—	76·6	25	—	—	814	—	—	·125[3]	1021	25	—	
·043	·0039	—	—	74·3	25	—	—	790	—	—	·25	956	25	—	
·086	·0078	—	—	71·6	25	—	—	761	—	—	·5	841	25	—	[2] At 25°.
·172	·0156	—	—	68·9	25	—	—	732	—	—	1·	649	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·343	·0312	—	—	66·0	25	—	—	701	—	—	—	—	—	—	

Lithium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COOLi, 94·02.

·0091	·000976	—	—	66·5[1]	25	—	—	707[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·0182	·00195	—	—	64·8	25	—	—	689	—	—	—	—	—	—	
·0365	·0039	—	—	63·0	25	—	—	670	—	—	—	—	—	—	
·073	·0078	—	—	60·7	25	—	—	645	—	—	—	—	—	—	
·146	·0156	—	—	58·4	25	—	—	621	—	—	—	—	—	—	[2] At 25°.
·293	·0312	—	—	55·6	25	—	—	591	—	—	—	—	—	—	

Lactic Acid.

Equivalent Gramme Molecule, $CH_3C(OH)HCOOH$, 90.

·0022	·000244	—	—	44·0[1]	25	—	—	1987[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 328.
·0044	·000488	—	—	33·8	25	—	—	1526	—	—	—	—	—	—	
·0088	·000976	—	—	26·0	25	—	—	1174	—	—	—	—	—	—	
·0175	·00195	—	—	19·5	25	—	—	881	—	—	—	—	—	—	
·035	·0039	—	—	14·4	25	—	—	650	—	—	—	—	—	—	[2] At 25°.
·070	·0078	—	—	10·6	25	—	—	479	—	—	—	—	—	—	

·140	·0156	—	—	7·6	25	—	—	343	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·280	·0312	—	—	5·5	25	—	—	248	—	—	—	—	—	—	
·560	·0625	—	—	3·9	25	—	—	177	—	—	·125[3]	1059	25	—	
1·122	·125	1·0026	25	2·8	25	—	—	125	—	—	·25	1032	25	—	
2·239	·25	1·0052	25	1·9	25	—	—	88	—	—	·5	976	25	—	
4·455	·5	1·0103	25	1·3	25	—	—	60	—	—	1·	874	25	—	

Potassium Lactate.

Equivalent Gramme Molecule, $CH_3C(OH)HCOOK$, 128·13.

·0125	·000976	—	—	102·6[1]	25	—	—	1091[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·025	·00195	—	—	99·9	25	—	—	1062	—	—	—	—	—	—	
·050	·0039	—	—	97·5	25	—	—	1036	—	—	—	—	—	—	
·100	·0078	—	—	94·8	25	—	—	1008	—	—	—	—	—	—	
·200	·0156	—	—	91·9	25	—	—	977	—	—	—	—	—	—	[2] At 25°.
·400	·0312	—	—	88·9	25	—	—	945	—	—	—	—	—	—	

Sodium Lactate.

Equivalent Gramme Molecule, $CH_3C(OH)HCOONa$, 112·04.

·0110	·000976	—	—	81·1[1]	25	—	—	862[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 100.
·0219	·00195	—	—	79·2	25	—	—	842	—	—	·125[3]	1039	25	—	
·0438	·0039	—	—	77·1	25	—	—	820	—	—	·25	990	25	—	
·0875	·0078	—	—	74·6	25	—	—	793	—	—	·5	893	25	—	[2] At 25°.
·175	·0156	—	—	71·9	25	—	—	764	—	—	1·	729	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·349	·0312	—	—	69·4	25	—	—	738	—	—	—	—	—	—	

Oxalic Acid.

Equivalent Gramme Molecule, $\frac{1}{2}(COOH)_2$, 45.

·0011	·000244	—	—	59·2[1]	25	—	—	2434	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 457.
·0022	·000488	—	—	49·3	25	—	—	2027	—	—	—	—	—	—	
·0044	·000976	—	—	46·0	25	—	—	1889	—	—	—	—	—	—	
·0088	·00195	—	—	43·6	25	—	—	1792	—	—	—	—	—	—	
·0175	·0039	—	—	41·8	25	—	—	1717	—	—	—	—	—	—	
·035	·0078	—	—	39·9	25	—	—	1638	—	—	—	—	—	—	
·070	·0156	—	—	37·5	25	—	—	1542	—	—	—	—	—	—	
·140	·0312	—	—	34·5	25	—	—	1417	—	—	—	—	—	—	

Oxalic Acid—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}(COOH)_2$, 45.

			°		°					°			°		
·280	·0625	—	—	30·7	25	—	—	1261	—	—	—	—	—	—	
·560	·125	—	—	26·4	25	—	—	1085	—	—	—	—	—	—	
—	·25	—	—	22·1	25	—	—	906	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·5	—	—	17·9	25	·0142	—	736	—	—	—	—	—	—	
—	1·	—	—	14·1	25	—	—	578	—	—	—	—	—	—	
·280	·0625	—	—	75·8[2]	18	—	1212	1288	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 49.
·560	·125	—	—	131·3	18	—	1050	1116	—	—	—	—	—	—	
—	·25	—	—	219·7	18	—	879	938	—	—	—	—	—	—	
—	·5	—	—	356·0	18	—	713	758	—	—	—	—	—	—	
·0009	·0002	—	—	185[3]	20	—	—	2331	—	—	—	—	—	—	
·009	·002	—	—	144	20	—	—	1814	—	—	—	—	—	—	
·045	·01	—	—	128	20	—	—	1609	—	—	—	—	—	—	
·090	·02	—	—	119	20	—	—	1506	—	—	—	—	—	—	
·180	·04	—	—	110	20	—	—	1381	—	—	—	—	—	—	

Potassium Oxalate.

Equivalent Gramme Molecule, $\frac{1}{2}(COOK)_2$, 83·13.

—	·5	—	—	373[1]	18	·0214	746	793	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
—	1·	—	—	688	18	·0209	688	730	—	—	—	—	—	—	
—	1·5	—	—	959	18	·0205	640	680	—	—	—	—	—	—	
19·3	—	—	—	—	—	—	—	—	·441[4]	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·0625	—	—	56[2]	18	—	896	953	—	—	—	—	—	—	
—	·125	—	—	106	18	—	848	901	—	—	—	—	—	—	
—	·25	—	—	198	18	—	792	842	—	—	—	—	—	—	
—	·5	—	—	368	18	—	736	782	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 50.
·0055	·00066	—	—	103·9[3]	20	—	—	1186	—	—	—	—	—	—	
·0068	·00082	—	—	103·7	20	—	—	1184	—	—	—	—	—	—	
·0274	·0033	—	—	98·4	20	—	—	1124	—	—	—	—	—	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 871.
·0548	·0066	—	—	94·9	20	·022	—	1084	—	—	—	—	—	—	

Tartaric Acid.

Equivalent Gramme Molecule, $\frac{1}{2}C_2H_2(OH)_2(COOH)_2$, 75.

·00182	·000244	—	—	94·8[1]	25	—	—	2140[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 340.
·00365	·000488	—	—	80·3	25	—	—	1813	—	—	—	—	—	—	
·0073	·000976	—	—	67·0	25	—	—	1513	—	—	—	—	—	—	
·0146	·00195	—	—	54·5	25	—	—	1230	—	—	—	—	—	—	
·0292	·0039	—	—	43·1	25	—	—	973	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 89.
·0585	·0078	—	—	33·1	25	—	—	747	—	—	—	—	—	—	
·117	·0156	—	—	25·1	25	—	—	567	—	—	—	—	—	—	
·234	·0312	—	—	18·7	25	—	—	422	—	—	—	—	—	—	
·468	·0625	1·0016	15	13·7	25	—	—	309	—	—	—	—	—	—	[3] At 25°.
·934	·125	1·0042	15	9·9	25	—	—	223	—	—	—	—	—	—	
1·86	·25	1·0083	15	7·1	25	—	—	160	—	—	—	—	—	—	
3·69	·5	1·0165	15	5·05	25	—	—	114	—	—	—	—	—	—	
7·26	1·	1·0334	15	3·46	25	—	—	78	—	—	—	—	—	—	
·0015	·0002	—	—	155[2]	17	—	—	2144	—	—	—	—	—	—	
·003	·0004	—	—	135	17	—	—	1867	—	—	—	—	—	—	
·015	·002	—	—	88	17	—	—	1224	—	—	—	—	—	—	
·030	·004	—	—	69·6	17	—	—	963	—	—	—	—	—	—	
·075	·01	—	—	49·4	17	·020	—	683	—	—	—	—	—	—	
·150	·02	—	—	37·0	17	—	—	512	—	—	—	—	—	—	

Benzoic Acid.

Equivalent Gramme Molecule, C_6H_5COOH, 122.

·00298	·000244	—	—	31·7[1]	25	—	—	1433[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 343.
·00595	·000488	—	—	24·6	25	—	—	1111	—	—	—	—	—	—	
·0119	·000976	—	—	18·4	25	—	—	832	—	—	—	—	—	—	
·0238	·00195	—	—	13·6	25	—	—	615	—	—	—	—	—	—	
·0475	·0039	—	—	9·95	25	—	—	449	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 44.
·095	·0078	—	—	7·20	25	—	—	325	—	—	—	—	—	—	
·190	·0156	—	—	5·20	25	—	—	235	—	—	—	—	—	—	
·00122	·0001	—	—	60·2[2]	17	—	—	833	—	—	—	—	—	—	[3] At 25°.
·0244	·002	—	—	44·4	17	—	—	614	—	—	—	—	—	—	
·061	·005	—	—	29·0	17	—	—	401	—	—	—	—	—	—	
·122	·01	—	—	20·8	17	·020	—	288	—	—	—	—	—	—	

Salicylic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

		°			°					°			°		
·0034	·000244	—	—	66·6[1]	25	—	—	3008[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 344.
·0068	·000488	—	—	59·9	25	—	—	2704	—	—	—	—	—	—	
·0135	·000976	—	—	51·2	25	—	—	2313	—	—	—	—	—	—	
·027	·00195	—	—	41·8	25	—	—	1886	—	—	—	—	—	—	
·054	·0039	—	—	32·3	25	—	—	1461	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 80.
·108	·0078	—	—	25·1	25	—	—	1135	—	—	—	—	—	—	
·216	·0156	—	—	19·1	25	—	—	863	—	—	—	—	—	—	
·0138	·001	—	—	171·2[2]	17	—	—	2367	—	—	—	—	—	—	
·0345	·0025	—	—	128·7	17	—	—	1780	—	—	—	—	—	—	[2] At 25°.
·069	·005	—	—	99·4	17	—	—	1375	—	—	—	—	—	—	
·138	·01	—	—	75·1	17	·020	—	1039	—	—	—	—	—	—	

Metaoxybenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

·0034	·000244	—	—	34·3[1]	25	—	—	1550[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 345.
·0068	·000488	—	—	26·8	25	—	—	1211	—	—	—	—	—	—	
·0135	·000976	—	—	20·3	25	—	—	918	—	—	—	—	—	—	
·027	·00195	—	—	15·2	25	—	—	686	—	—	—	—	—	—	
·054	·0039	—	—	11·2	25	—	—	507	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 82.
·108	·0078	—	—	8·24	25	—	—	372	—	—	—	—	—	—	
·216	·0156	—	—	5·99	25	—	—	271	—	—	—	—	—	—	
·432	·0312	—	—	4·31	25	—	—	195	—	—	—	—	—	—	
·0138	·001	—	—	71·9[2]	17	—	—	994	—	—	—	—	—	—	[2] At 25°.
·0345	·0025	—	—	48·1	17	—	—	663	—	—	—	—	—	—	
·069	·005	—	—	35·0	17	—	—	484	—	—	—	—	—	—	
·138	·01	—	—	25·2	17	·020	—	349	—	—	—	—	—	—	

Paroxybenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

·0034	·000244	—	—	22·8[1]	25	—	—	1020[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 845.
·0068	·000488	—	—	17·2	25	—	—	776	—	—	—	—	—	—	
·0135	·000976	—	—	12·7	25	—	—	573	—	—	—	—	—	—	
·027	·00195	—	—	9·2	25	—	—	416	—	—	—	—	—	—	[2] At 25°.

·054	·0039	—	—	6·65	25	—	—	300	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 84.
·108	·0078	—	—	4·77	25	—	—	215	—	—	—	—	—	—	
·216	·0156	—	—	3·38	25	—	—	153	—	—	—	—	—	—	
·432	·0312	—	—	2·39	25	—	—	108	—	—	—	—	—	—	
·0138	·001	—	—	42·6[3]	17	—	—	589	—	—	—	—	—	—	
·0345	·0025	—	—	28·0	17	—	—	387	—	—	—	—	—	—	
·069	·005	—	—	20·0	17	—	—	276	—	—	—	—	—	—	
·138	·01	—	—	14·3	17	·020	—	198	—	—	—	—	—	—	

ORTHONITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	72·6[1]	25	—	—	3280[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 347.
·0081	·000488	—	—	70·9	25	—	—	3203	—	—	—	—	—	—	
·0162	·000976	—	—	67·2	25	—	—	3037	—	—	—	—	—	—	
·0325	·00195	—	—	61·8	25	—	—	2789	—	—	—	—	—	—	[2] At 25°.
·065	·0039	—	—	54·3	25	—	—	2453	—	—	—	—	—	—	
·130	·0078	—	—	45·9	25	—	—	2073	—	—	—	—	—	—	
·260	·0156	—	—	37·4	25	—	—	1688	—	—	—	—	—	—	
·521	·0312	—	—	29·3	25	—	—	1321	—	—	—	—	—	—	

METANITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	53·4[1]	25	—	—	2410[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 347.
·0081	·000488	—	—	44·7	25	—	—	2021	—	—	—	—	—	—	
·0162	·000976	—	—	35·8	25	—	—	1616	—	—	—	—	—	—	
·0325	·00195	—	—	27·7	25	—	—	1250	—	—	—	—	—	—	[2] At 25°.
·065	·0039	—	—	20·8	25	—	—	934	—	—	—	—	—	—	
·130	·0078	—	—	15·3	25	—	—	691	—	—	—	—	—	—	
·260	·0156	—	—	11·2	25	—	—	505	—	—	—	—	—	—	

PARANITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	54·6[1]	25	—	—	2464[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 348.
·0081	·000488	—	—	45·8	25	—	—	2069	—	—	—	—	—	—	
·0162	·000976	—	—	37·1	25	—	—	1676	—	—	—	—	—	—	
·0325	·00195	—	—	28·9	25	—	—	1307	—	—	—	—	—	—	[2] At 25°.

Orthochlorbenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4ClCOOH$, 156·46.

			°		°				°				°		
·0038	·000244	—	—	67·4[1]	25	—	—	3046[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 349.
·0076	·000488	—	—	61·9	25	—	—	2794	—	—	—	—	—	—	
·0152	·000976	—	—	53·8	25	—	—	2431	—	—	—	—	—	—	
·0305	·00195	—	—	44·7	25	—	—	2018	—	—	—	—	—	—	
·061	·0039	—	—	35·5	25	—	—	1605	—	—	—	—	—	—	[2] At 25°.
·122	·0078	—	—	27·6	25	—	—	1246	—	—	—	—	—	—	

Metachlorbenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4ClCOOH$, 156·46.

·0038	·000244	—	—	43·6[1]	25	—	—	1971[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 349.
·0076	·000488	—	—	34·9	25	—	—	1577	—	—	—	—	—	—	
·0152	·000976	—	—	20·9	25	—	—	946	—	—	—	—	—	—	
·0305	·00195	—	—	20·4	25	—	—	921	—	—	—	—	—	—	
·061	·0039	—	—	15·1	25	—	—	683	—	—	—	—	—	—	[2] At 25°.

Potassic Hydrate.

Equivalent Gramme Molecule, KHO, 56·13.

·000056	·00001	—	—	—	18	—	747[1]	794	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000112	·00002	—	—	—	18	—	845	898	—	—	—	—	—	—	
·000336	·00006	—	—	—	18	—	1474	1567	—	—	—	—	—	—	
·000561	·0001	—	—	—	18	—	1689	1795	—	—	—	—	—	—	
·00112	·0002	—	—	—	18	—	1892	2011	—	—	—	—	—	—	[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 353.
·00336	·0006	—	—	—	18	—	2074	2205	—	—	—	—	—	—	
·00561	·001	—	—	—	18	—	2110	2243	—	—	—	—	—	—	
·0112	·002	—	—	—	18	—	2140	2275	—	—	—	—	—	—	
·0336	·006	—	—	—	18	—	2141	2276	—	—	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·0561	·01	—	—	—	18	·0194	2124	2258	—	—	—	—	—	—	
·168	·03	—	—	—	18	—	2078	2209	—	—	—	—	—	—	
·280	·05	1·0019	15	—	18	—	2045	2174	—	—	—	—	—	—	
·558	·1	1·0047	15	—	18	—	1980	2111	—	—	—	—	—	—	[4] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·103	—	—	—	—	—	—	—	·742[4]	—	—	—	—	—	
—	·190	—	—	—	—	—	—	—	·730	—	—	—	—	—	
2·743	·5	1·0230	15	—	18	·0188	1841	1957	—	—	—	—	—	—	
—	·804	—	—	—	—	—	—	—	·739	—	—	—	—	—	
5·376	1·	1·0440	15	—	18	·0187	1718	1826	—	—	—	—	—	—	

14·93	3·	1·1274	15	—	18	·0191	1314	1397	—	—	—	—	—	—	
23·17	5·	1·2109	15	—	18	·0204	990	1052	—	—	—	—	—	—	
39·83	10·	1·4091	15	—	18	·0273	423	450	—	—	—	—	—	—	
·0055	·000975	—	—	228·8[2]	25	—	—	2141	—	—	—	—	—	—	
·0109	·00195	—	—	231·2	25	—	—	2164	—	—	—	—	—	—	
·0219	·00390	—	—	233·1	25	—	—	2181	—	—	—	—	—	—	
·0438	·0078	—	—	232·6	25	—	—	2177	—	—	—	—	—	—	
·0875	·0156	—	—	230·7	25	—	—	2158	—	—	—	—	—	—	
·175	·0312	—	—	228·9	25	—	—	2142	—	—	—	—	—	—	
·350	·0625	1·0026	15	225·3	25	—	—	2108	—	—	—	—	—	—	
·697	·125	1·0061	15	220·2	25	—	—	2063	—	—	—	—	—	—	
1·386	·25	1·0121	15	214·6	25	—	—	2008	—	—	—	—	—	—	
2·743	·5	1·0230	15	206·4	25	—	—	1932	—	—	—	—	—	—	
·238	·0424	—	—	82·5[2]	18	—	1946	2069	—	—	—	—	—	—	
·457	·0816	—	—	158	18	—	1938	2060	—	—	—	—	—	—	
·575	·103	1·0049	15	210	18	—	2039	2162	—	—	—	—	—	—	
·857	·1537	1·0077	15	292	18	—	1900	2020	—	—	—	—	—	—	
1·146	·206	1·0101	15	408	18	—	1980	2105	—	—	—	—	—	—	
2·272	·412	1·0191	15	786	18	—	1908	2028	—	—	—	—	—	—	
4·467	·825	1·0367	15	1470	18	—	1782	1894	—	—	—	—	—	—	

Sodic Hydrate.

Equivalent Gramme Molecule, NaOH, 40·04.

1·954	·5	1·0225	15	817[1]	18	·0194	1634	1737	—	—	—	—	—	—	
3·828	1·	1·0441	15	1488	18	·0199	1488	1581	—	—	—	—	—	—	
7·366	2·	1·0850	15	2447	18	·0209	1223	1300	—	—	—	—	—	—	
10·68	3·	1·1224	15	3020	18	·0221	1007	1070	—	—	—	—	—	—	
13·81	4·	1·1569	15	3264	18	·0241	816	867	—	—	—	—	—	—	
16·79	5·	1·1896	15	3259	18	·0266	652	693	—	—	—	—	—	—	
30·	10·	1·3320	15	1896	18	·0452	190	202	—	—	—	—	—	—	
·00385	·000975	—	—	211·6[2]	25	—	—	1980	—	—	—	—	—	—	
·0077	·00195	—	—	215·1	25	—	—	2013	—	—	—	—	—	—	
·0155	·0039	—	—	216·7	25	—	—	2028	—	—	—	—	—	—	
·0311	·0078	—	—	215·2	25	—	—	2011	—	—	—	—	—	—	
·0622	·0156	—	—	212·4	25	—	—	1988	—	—	—	—	—	—	
·124	·0312	—	—	210·7	25	—	—	1972	—	—	—	—	—	—	
·248	·0625	1·0023	15	205·0	25	—	—	1918	—	—	—	—	—	—	

[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.

[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 355.

Sodic Hydrate—*continued.*

Equivalent Gramme Molecule, NaOH, 40·04.

—	·108	—	—	—	—	—	—	—	·843[4]	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·495	·125	1·0055	15	199·3	25	—	—	1865	—	—	—	—	—	
·986	·25	1·0120	15	191·0	25	—	—	1787	—	—	—	—	—	
—	·285	—	—	—	—	—	—	—	·800	—	—	—	—	
1·954	·5	1·0225	15	181·6	25	—	—	1691	—	—	—	—	—	[4] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	1·084	—	—	—	—	—	—	—	·827	—	—	—	—	
·127	·0319	—	15	56·7[3]	18	—	1777	1889	—	—	—	—	—	
·240	·0602	1·0022	15	106	18	—	1760	1871	—	—	—	—	—	
·501	·1257	1·0056	15	217	18	—	1722	1830	—	—	—	—	—	
·642	·1618	1·0074	15	287	18	—	1771	1883	—	—	—	—	—	
1·012	·2564	1·0121	15	424	18	—	1515	1610	—	—	—	—	—	
1·274	·3237	1·0150	15	548	18	—	1691	1797	—	—	—	—	—	
2·515	·6474	1·0286	15	1022	18	—	1579	1678	—	—	—	—	—	
4·893	1·2947	1·0576	15	1805	18	—	1394	1481	—	—	—	—	—	

Lithium Hydrate.

Equivalent Gramme Molecule, LiOH, 24·02.

·0023	·000976	—	—	204·4[1]	25	—	—	1913	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 856.
·0047	·00195	—	—	206·3	25	—	—	1931	—	—	—	—	—	
·0094	·0039	—	—	206·8	25	—	—	1935	—	—	—	—	—	
·0188	·0078	—	—	205·9	25	—	—	1927	—	—	—	—	—	
·0375	·0156	—	—	202·2	25	—	—	1892	—	—	—	—	—	
·075	·0312	—	—	199·6	25	·0194	—	1868	—	—	—	—	—	[2] Kohlrausch, *Wied. Annal.* vol. vi. p. 151.
·150	·0625	—	—	193·8	25	—	—	1814	—	—	—	—	—	
·300	·125	—	—	186·5	25	—	—	1745	—	—	—	—	—	
—	·25	—	—	179·2	25	—	—	1677	—	—	—	—	—	[3] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·201	—	—	—	—	—	—	—	·857[3]	—	—	—	—	
—	·402	—	—	—	—	—	—	—	·863	—	—	—	—	
—	·5	—	—	694[2]	18	·0191	1388	1475	—	—	—	—	—	
—	1·	—	—	1253	18	·0196	1253	1332	—	—	—	—	—	
—	1·495	—	—	—	—	—	—	—	·890	—	—	—	—	
—	2·	—	—	2108	18	·0202	1054	1120	—	—	—	—	—	
—	3·	—	—	2660	18	·0215	887	943	—	—	—	—	—	

Barium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ba(OH)_2$, 85·5.

·0083	·000976	—	—	218·4[1]	25	—	—	2322[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0166	·00195	—	—	219·8	25	—	—	2336	—	—	—	—	—	—	
·0332	·0039	—	—	218·7	25	—	—	2325	—	—	—	—	—	—	
·0665	·0078	—	—	215·9	25	—	—	2295	—	—	—	—	—	—	[2] At 25°.
·133	·0156	—	—	210·3	25	—	—	2235	—	—	—	—	—	—	
·266	·0312	—	—	201·0	25	—	—	2137	—	—	—	—	—	—	
·532	·0625	—	—	192·3	25	—	—	2044	—	—	—	—	—	—	
—	·125	—	—	183·9	25	—	—	1955	—	—	—	—	—	—	
—	·25	—	—	174·4	25	—	—	1854	—	—	—	—	—	—	

Strontium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Sr(OH)_2$, 60·75.

·0059	·000976	—	—	209·2[1]	25	—	—	2224[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0118	·00195	—	—	212·2	25	—	—	2256	—	—	—	—	—	—	
·0236	·0039	—	—	211·7	25	—	—	2250	—	—	—	—	—	—	
·0472	·0078	—	—	209·0	25	—	—	2222	—	—	—	—	—	—	[2] At 25°.
·0945	·0156	—	—	202·5	25	—	—	2152	—	—	—	—	—	—	
·189	·0312	—	—	196·5	25	—	—	2089	—	—	—	—	—	—	
·378	·0625	—	—	190·1	25	—	—	2021	—	—	—	—	—	—	

Calcium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ca(OH)_2$, 37.

·0036	·000976	—	—	213·2[1]	25	—	—	2266[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0072	·00195	—	—	215·4	25	—	—	2290	—	—	—	—	—	—	
·0144	·0039	—	—	213·4	25	—	—	2268	—	—	—	—	—	—	
·0288	·0078	—	—	209·3	25	—	—	2225	—	—	—	—	—	—	[2] At 25°.
·0575	·0156	—	—	200·2	25	—	—	2128	—	—	—	—	—	—	
·115	·0312	—	—	190·5	25	—	—	2025	—	—	—	—	—	—	

Ammonia.

Equivalent Gramme Molecule, NH_3, 17·04.

·000017	·00001	—	—	—	18	—	560[1]	595	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 197.
·000034	·00002	—	—	—	18	—	700	744	—	—	—	—	—	—	
·000102	·00006	—	—	—	18	—	690	733	—	—	—	—	—	—	

Ammonia—*continued.*

Equivalent Gramme Molecule, NH_3, 17·04.

			°		°					°				°		
·00017	·0001	—	—	—	18	—	610	648	—	—	—	—	—	—	—	[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 358.
·00034	·0002	—	—	—	18	—	500	531	—	—	—	—	—	—	—	
·00102	·0006	—	—	—	18	—	330	351	—	—	—	—	—	—	—	
·0017	·001	—	—	—	18	—	260	276	—	—	—	—	—	—	—	
·0034	·002	—	—	—	18	—	190	202	—	—	—	—	—	—	—	
·0102	·006	—	—	—	18	—	116	123	—	—	—	—	—	—	—	[3] At 25°.
·017	·01	—	—	—	18	—	92	98	—	—	—	—	—	—	—	
·051	·03	—	—	—	18	—	50	53	—	—	—	—	—	—	—	
·085	·05	—	—	—	18	—	43	46	—	—	—	—	—	—	—	
·17	·1	—	—	—	18	—	31	33	—	—	—	—	—	—	—	
·85	·5	—	—	—	18	—	12	12·7	—	—	—	—	—	—	—	
1·71	1·	·9928	16	—	18	—	8·4	8·9	—	—	—	—	—	—	—	
5·22	3·	·9776	16	—	18	—	3·3	3·5	—	—	—	—	—	—	—	
—	5·	—	—	—	18	—	2·4	2·5	—	—	—	—	—	—	—	
—	10·	—	—	—	18	—	·5	·53	—	—	—	—	—	—	—	
·00165	·000975	—	—	37·0[2]	25	—	—	393[3]	—	—	—	—	—	—	—	
·0033	·00195	—	—	25·8	25	—	—	274	—	—	—	—	—	—	—	
·0066	·0039	—	—	17·9	25	—	—	189	—	—	—	—	—	—	—	
·0132	·0078	—	—	12·4	25	—	—	132	—	—	—	—	—	—	—	
·0265	·0156	—	—	8·7	25	—	—	92	—	—	—	—	—	—	—	
·053	·0312	—	—	6·13	25	—	—	65	—	—	—	—	—	—	—	
·106	·0625	—	—	4·27	25	—	—	45	—	—	—	—	—	—	—	
·212	·125	—	—	3·01	25	—	—	32	—	—	—	—	—	—	—	
·425	·25	—	—	2·10	25	—	—	22	—	—	—	—	—	—	—	
·85	·5	—	—	1·46	25	—	—	15·5	—	—	—	—	—	—	—	

Methylamine.

Equivalent Gramme Molecule, CH_3NH_2, 31·04.

·00305	·000976	—	—	108·0[1]	25	—	—	1148[2]	—	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 360.
·0061	·00195	—	—	84·7	25	—	—	900	—	—	—	—	—	—	—	
·0122	·0039	—	—	64·8	25	—	—	689	—	—	—	—	—	—	—	
·0245	·0078	—	—	49·0	25	—	—	521	—	—	—	—	—	—	—	
·049	·0156	—	—	36·2	25	—	—	385	—	—	—	—	—	—	—	[2] At 25°.

·098	·0312	—	—	26·4	25	—	—	281	—	—	—	—	—	—	
·195	·0625	—	—	19·1	25	—	—	204	—	—	—	—	—	—	
·39	·125	—	—	13·5	25	—	—	144	—	—	—	—	—	—	
·78	·25	—	—	9·5	25	—	—	101	—	—	—	—	—	—	
—	·5	—	—	6·4	25	—	—	68	—	—	—	—	—	—	

Ethylamine.

Equivalent Gramme Molecule, $C_2H_5NH_2$, 45·04.

·0044	·000976	—	—	112·0[1]	25	—	—	1190[2]	—	—	—	—	—	—	
·0088	·00195	—	—	88·0	25	—	—	936	—	—	—	—	—	—	
·0175	·0039	—	—	66·9	25	—	—	711	—	—	—	—	—	—	
·035	·0078	—	—	50·2	25	—	—	533	—	—	—	—	—	—	
·070	·0156	—	—	36·9	25	—	—	393	—	—	—	—	—	—	
·140	·0312	—	—	26·8	25	—	—	285	—	—	—	—	—	—	
·281	·0625	—	—	19·3	25	—	—	205	—	—	—	—	—	—	
·562	·125	—	—	13·5	25	—	—	144	—	—	—	—	—	—	
1	·25	—	—	9·3	25	—	—	99	—	—	—	—	—	—	
—	·5	—	—	6·1	25	—	—	64	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 360.

[2] At 25°.

Propylamine.

Equivalent Gramme Molecule, $C_3H_7NH_2$, 59·04.

·0042	·000976	—	—	97·7[1]	25	—	—	1038[2]	—	—	—	—	—	—	
·0084	·00195	—	—	77·2	25	—	—	821	—	—	—	—	—	—	
·0169	·0039	—	—	59·2	25	—	—	629	—	—	—	—	—	—	
·0338	·0078	—	—	44·3	25	—	—	471	—	—	—	—	—	—	
·0675	·0156	—	—	32·6	25	—	—	347	—	—	—	—	—	—	
·135	·0312	—	—	23·7	25	—	—	252	—	—	—	—	—	—	
·37	·0625	—	—	16·9	25	—	—	180	—	—	—	—	—	—	
·74	·125	—	—	11·9	25	—	—	127	—	—	—	—	—	—	
—	·25	—	—	8·1	25	—	—	86	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 361.

[2] At 25°.

Isobutylamine.

Equivalent Gramme Molecule, $C_4H_9NH_2$, 73·04.

·0071	·000976	—	—	82·3[1]	25	—	—	875[2]	—	—	—	—	—	—	
·0142	·00195	—	—	64·5	25	—	—	686	—	—	—	—	—	—	
·0285	·0039	—	—	49·2	25	—	—	523	—	—	—	—	—	—	
·057	·0078	—	—	36·6	25	—	—	389	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 361.

[2] At 25°.

ISOBUTYLAMINE—*continued.*

Equivalent Gramme Molecule, $C_4H_9NH_2$, 73·04.

			°		°					°				°	
·114	·0156	—	—	26·9	25	—	—	286	—	—	—	—	—	—	
·228	·0312	—	—	19·4	25	—	—	207	—	—	—	—	—	—	
·455	·0625	—	—	13·8	25	—	—	147	—	—	—	—	—	—	
·91	·125	—	—	9·6	25	—	—	103	—	—	—	—	—	—	
—	·25	—	—	6·4	25	—	—	69	—	—	—	—	—	—	

AMYLAMINE.

Equivalent Gramme Molecule, $C_5H_{11}NH_2$, 87·04.

·0085	·000976	—	—	97·5[1]	25	—	—	1036[2]	—	—	—	—	—	—	
·017	·00195	—	—	77·4	25	—	—	823	—	—	—	—	—	—	
·034	·0039	—	—	59·9	25	—	—	637	—	—	—	—	—	—	
·068	·0078	—	—	44·4	25	—	—	472	—	—	—	—	—	—	
·136	·0156	—	—	33·2	25	—	—	354	—	—	—	—	—	—	
·272	·0312	—	—	24·2	25	—	—	257	—	—	—	—	—	—	
·544	·0625	—	—	17·2	25	—	—	183	—	—	—	—	—	—	
—	·125	—	—	11·9	25	—	—	127	—	—	—	—	—	—	
—	·25	—	—	7·9	25	—	—	84	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 362.

[2] At 25°.

DIMETHYLAMINE.

Equivalent Gramme Molecule, $(CH_3)_2NH$, 45·04.

·0044	·000976	—	—	120·7[1]	25	—	—	1283[2]	—	—	—	—	—	—	
·0088	·00195	—	—	95·7	25	—	—	1017	—	—	—	—	—	—	
·0175	·0039	—	—	73·9	25	—	—	786	—	—	—	—	—	—	
·035	·0078	—	—	55·9	25	—	—	595	—	—	—	—	—	—	
·070	·0156	—	—	41·6	25	—	—	442	—	—	—	—	—	—	
·140	·0312	—	—	30·4	25	—	—	323	—	—	—	—	—	—	
·281	·0625	—	—	21·8	25	—	—	232	—	—	—	—	—	—	
·562	·125	—	—	15·4	25	—	—	164	—	—	—	—	—	—	
—	·25	—	—	10·6	25	—	—	113	—	—	—	—	—	—	
—	·5	—	—	6·9	25	—	—	73	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 363.

[2] At 25°.

Diethylamine.

Equivalent Gramme Molecule, $(C_2H_5)_2NH$, 73·04.

·0071	·000976	—	—	130·3[1]	25	—	—	1382[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 363.
·0142	·00195	—	—	108·4	25	—	—	1152	—	—	—	—	—	—	
·0285	·0039	—	—	85·9	25	—	—	913	—	—	—	—	—	—	
·057	·0078	—	—	65·8	25	—	—	699	—	—	—	—	—	—	[2] At 25°.
·114	·0156	—	—	49·4	25	—	—	525	—	—	—	—	—	—	
·228	·0312	—	—	36·1	25	—	—	384	—	—	—	—	—	—	
·455	·0625	—	—	26·0	25	—	—	277	—	—	—	—	—	—	
·910	·125	—	—	18·2	25	—	—	193	—	—	—	—	—	—	
—	·25	—	—	12·3	25	—	—	131	—	—	—	—	—	—	

Trimethylamine.

Equivalent Gramme Molecule, $(CH_3)_3N$, 59·04.

·0058	·000976	—	—	56·81[1]	25	—	—	604[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 364.
·0116	·00195	—	—	42·8	25	—	—	455	—	—	—	—	—	—	
·0231	·0039	—	—	32·2	25	—	—	342	—	—	—	—	—	—	
·0462	·0078	—	—	23·7	25	—	—	252	—	—	—	—	—	—	[2] At 25°.
·0925	·0156	—	—	17·3	25	—	—	183	—	—	—	—	—	—	
·185	·0312	—	—	12·5	25	—	—	132	—	—	—	—	—	—	
·370	·0625	—	—	8·9	25	—	—	94	—	—	—	—	—	—	
·740	·125	—	—	6·2	25	—	—	66	—	—	—	—	—	—	
—	·25	—	—	4·2	25	—	—	44	—	—	—	—	—	—	
—	·5	—	—	2·63	25	—	—	28	—	—	—	—	—	—	

Triethylamine.

Equivalent Gramme Molecule, $(C_2H_5)_3N$, 101·04.

·0099	·000976	—	—	111·6[1]	25	—	—	1186[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 364.
·0198	·00195	—	—	87·6	25	—	—	931	—	—	—	—	—	—	
·0395	·0039	—	—	66·6	25	—	—	708	—	—	—	—	—	—	
·079	·0078	—	—	49·7	25	—	—	528	—	—	—	—	—	—	[2] At 25°.
·158	·0156	—	—	36·4	25	—	—	387	—	—	—	—	—	—	
·315	·0312	—	—	26·1	25	—	—	277	—	—	—	—	—	—	
·630	·0625	—	—	18·5	25	—	—	196	—	—	—	—	—	—	
—	·125	—	—	12·6	25	—	—	134	—	—	—	—	—	—	
—	·25	—	—	8·2	25	—	—	88	—	—	—	—	—	—	
—	·5	—	—	4·8	25	—	—	51	—	—	—	—	—	—	

INDEX.

(*The numbers refer to the pages.*)

A.

ABBOT and NOYES, solubility and dissociation...187
ABEGG, freezing points of solutions...72, 213
Absorption of gases by liquids...10
,, coefficient...13
Accumulators...113
Acetic acid, conductivity of solutions of...140, 142
,, vapour pressure of solutions in...82
Acids, affinity of...162
,, conductivity of...149
Additive properties of salt solutions...174
ADIE, osmotic pressure...39
Affinity, chemical...152, 162, 164, 182, 189
Alcohols, vapour pressure of mixtures with water...98
Alcoholic solutions...142, 203, 205
ALEXEJEFF, mutual solubility of liquids...16
Alloys, melting points of...73
Alternating currents, use of...145
AMAGAT, deviation of air from the gaseous laws...70
Amalgams, freezing points of...73
,, vapour pressures of...93
Ammonia, conductivity of solutions of...150
,, solubility of...14
Applications of Electrolysis...131
ARMSTRONG, theory of solution...207

ARRHENIUS, conductivity and chemical affinity...162
,, ,, ,, osmotic pressure...166
,, diffusion of electrolytes...195
,, dissociation theory of electrolysis...155, 171, 184, 187
,, freezing points...213
,, heats of ionisation...192
,, isohydric solutions...186
,, temperature of maximum conductivity...194
,, vapour pressures of solutions...74
Avogadro's law, application to solutions...38, 40

B.

BECKMANN, freezing points...61, 67
,, vapour pressures and boiling points...90, 93
BECQUEREL, preparation of chemical compounds by electrolysis...131
BEETZ, resistance of electrolytes...144
BERTHELOT and JUNGFLEISCH, solubility in mixed liquids...31
BERZELIUS and HISINGER, electrolysis of salt solutions...105
,, theory of chemical action...127
Bichromate group, ionic velocity of the,...142
BLAGDEN, freezing points of solutions...54
Boiling points of solutions...85, 90
BOUTY, resistance of electrolytes...144
Boyle's law for solutions...27, 36, 40
BREDIG, influence of concentration in osmotic pressure...69
BUNSEN, absorption coefficients...13

C.

Cadmium iodide, electrolysis of alcoholic solutions of...132, 135
Calcium oxalate, decomposition of...163
,, sulphate, solubility of...21
CALLENDAR, platinum thermometer...62
Capacity of solvent, specific inductive...156, 204
,, electrostatic...146
CARLISLE and NICHOLSON, decomposition of water...104
Cell sap, motion of, and osmotic pressure...37
Cells, concentration...198
,, voltaic...103, 113, 114, 122, 198
Chemical affinity...152, 162, 178, 182, 184, 187
,, decomposition by electrolysis...104, 127

Chemical equilibrium...152, 180, 186, 187, 189
„ interchanges in solutions...106, 151, 173
„ theory of solution...12, 22, 206, 210, 211
Clausius, theory of electrolysis...151
Cobalt salts in solution...175
Coefficient of ionisation...157, 166, 168, 181, 187, 204
Colligative properties...42
Colloids...53
Concentration, its influence on conductivity...154, 157
„ „ „ freezing points...67
„ „ „ vapour pressures...92
„ cells...198
Conductivity of electrolytes...135, 143
„ „ and chemical affinity...162
„ „ „ osmotic pressure...165
Connection between electrical and other properties of solutions...162
Contact difference of potential...116, 121, 160, 197
Copper, deposition from solution...131
„ ion, velocity of the...142
„ sulphate, electrolysis of...132, 134
Coppet, freezing points of solutions...54
Cruickshank, electrolysis of salt solutions...104
Cryohydrates...72
Crystalloids...53
Czapski, theory of primary cell...125

D.

Dalton, solutions of liquids in gases...9
Daniell, electrolysis of sodium sulphate...128
„ primary cell...115, 125
Davy, electrochemical researches...104, 105, 107
Definition of the term "Solution"...6, 7
Densities of salt solutions...174
De Vries, isotonic solutions...37
Dialysis...53
Dielectric constant of solvent...156, 204
"Differentiation" curves...208
Diffusion...32, 45, 179, 194
„ constants...47, 50, 53, 197
„ experiments on...49

Diffusion of electrolytes...179, 194
,, through liquids...45
Dissociation theory of electrolysis...154, 155, 171, 180, 187, 211
Distillation of mixed liquids...99
Donders and Hamburger, variation of osmotic pressure with temperature...36
Double decomposition in solutions...106, 151, 173, 184, 187, 189
Double layer of electricity...119, 161

E.

Electrical double layer...119, 161
,, endosmose...159
,, properties of solutions...103, 127, 143, 162
Electrolysis, practical applications...131
,, theories of...170
Electrolytes, conduction by...113
,, conductivity of...143
,, diffusion of...179, 194
,, freezing points of...67
,, osmotic pressures of...38
,, vapour pressures of...92
Electrometers, Lippmann's...118
Electromotive force of contact...116, 121, 197
,, ,, polarisation...112, 144, 146
,, ,, primary cells...122, 198
Electroplating &c....131
Endosmose, electrical...159
Engel and Étard, influence of temperature on solubility...23
Equilibrium of saturated solutions...19, 21
,, at the melting point...29
,, chemical...152, 180, 184, 187, 189
Étard and Engel, influence of temperature on solubility...23
Evaporation, analogy with solution...25
Eykman, freezing points...60, 67

F.

Faraday, electrochemical researches...105 to 117
,, laws of electrolysis...108
Fick, theory of diffusion...47, 50

Films, resistance of liquid...158
FITZGERALD, ionisation...156
,, osmotic pressure...42
,, and TROUTON, Ohm's law for electrolytes...151
FITZPATRICK, electro-chemical properties of solutions...134, *Appendix*
,, measurement of resistance of electrolytes...147
,, function of the solvent...203
Fluidity, ionic...193, 202
Forces acting on the ions...138, 156, 205
Freezing points of solutions...4, 54, 168, 213
,, ,, ,, connection with conductivities...165, 171
,, ,, ,, ,, ,, osmotic pressures...55
,, ,, ,, ,, ,, vapour pressures...84
,, ,, ,, experiments on...54, 61, 168, 213
Friction coefficients, ionic...138
Fused salts, electrolysis of...105

G.

Gas constant...41
Gaseous laws, application to solutions...35, 40
Gases, discharge through...105
,, solutions in...8
,, solutions in liquids...10, 94
,, ,, ,, salt solutions...15
GALITZINE, solutions of liquids in gases...9
Gay Lussac's law, application to solutions...36, 40
GLADSTONE, properties of salt solutions...177
Graduation of thermometers...4
GRAHAM, experiments on diffusion...49, 52, 53
Gram-molecule, definition of...38
GROTTHUS, theory of electrolysis...106
GROVE, gas battery...114
,, primary cell...115
GULDBERG and WAAGE, chemical equilibrium...152, 189
GUTHRIE, cryohydrates...72

H.

HAMBURGER and DONDERS, influence of temperature on osmotic pressure... 36
Heat capacity of solutions...177, 209
,, effects of chemical action...162, 189, 192

Heat, effects of, solution and dilution...8, 12, 28, 209
,, of ionisation...190, 206
Helmholtz, von, contact difference of potential...118, 160
,, ,, electrical endosmose...160
,, ,, theory of primary cell...125
Henry, law of solution of gases ..13
Hess, law of thermo-neutrality...189
Heycock and Neville, melting points of alloys...73
Heydweiler and Kohlrausch, conductivity of pure water...201
Hisinger and Berzelius, electrolysis of salt solutions...105
Hittorf, conductivity and chemical activity...162
,, ,, of mixed solutions...180
,, migration of the ions...133, 134
,, nature of the ions...128
Horsford, resistance of electrolytes...144
Hydrate theory of solution...12, 22, 206, 210, 211
Hydrochloric acid, solutions of...10, 14, 96, 102
Hydrogen ion, velocity of the...140, 142
Hydrolytic dissociation...202

I.

Indicators, theory of...176
Induction, self, with alternating currents...146
Inductive capacity, specific, of solvent...156, 204
Ionisation...156, 166, 170, 181, 190, 204
,, power of solvents...156, 204
Ionic fluidity...193, 202
Ions, combination with solvent...156, 205
,, concentration of...180, 185, 187
,, electrical charges on...111, 136, 178, 195, 204
,, freedom of...106, 138, 151, 155, 171, 178
,, friction coefficients of...138
,, function of, in chemical change...153, 162, 184, 187
,, heats of, formation of...190, 206
,, migration of...132, 179
,, nature of...108, 127
,, velocities of...135, 138, 140, 154, 173, 196
Isohydric solutions...186
Isotonic solutions...37
,, coefficients...38

J.

JAHN, contact difference of potential...117
,, theory of primary cell...125
JONES, freezing points of solutions...69, 168, 213
JUNGFLEISCH and BERTHELOT, solubility in mixed liquids...31

K.

KELVIN, Lord, theory of primary cell...123
KOHLRAUSCH, coefficient of ionisation...157
,, conductivity of electrolytes...135, 145, 148
,, ,, of pure water...129, 149, 201
,, velocities of the ions...135, 173
KONOWALOFF, vapour pressures of mixed liquids...97

L.

LAMB, electrical endosmose...161
LIPPMANN, contact difference of potential...117
Liquid films, resistance of...158
Liquids, solutions of, in gases...9
,, ,, of, in liquids...16, 97
,, ,, of gases in...10, 94
,, ,, solids in...17
LIVEING, chemical equilibrium of solution...25
LODGE, velocities of the ions...140
LOEB and NERNST, migration of the ions...184
LOOMIS, freezing points of solutions...168, 213

M.

Magnesium hydroxide, formation of...202
Mass action, law of...152, 180, 184
Maximum conductivity, temperature of...193
Membranes, diffusion through...53
,, semipermeable...34, 179
MENDELÉEFF, properties of solutions...208
Mercury-dropping electrode...120
Methyl acetate, decomposition of...163
Migration of the ions...132, 179
,, constants...135

Mixed liquids...16, 97
,, ,, solubility in...31
,, solutions, dissociation of...184, 187
Mixtures, electrolysis of...130
,, solubility of...29, 187
Molecular conductivity...136, 149, 181
,, interchanges in solution...106, 151, 162, 173
,, volumes...174, 209

N.

Nernst, contact difference of potential...121, 197
,, dissociation theory...171, 186, 194
,, diffusion through liquids...46, 194
,, solubility of mixtures...30, 186
,, ,, in mixed liquids...31
,, and Abegg, freezing points...213
,, and Loeb, migration of the ions...134
Neutralisation of acids and bases...163, 175, 189, 192
Neville and Heycock, melting points of alloys...73
Nicholson and Carlisle, decomposition of water...104
Nicol, volume changes...175
Noyes, influence of concentration on osmotic pressure...69
,, and Abbot, solubility and dissociation...187

O.

Ohm's law for electrolytes...143, 151
Osmotic pressure...32, 34, 39, 206
,, ,, and conductivity...165
,, ,, ,, freezing point...55, 67
,, ,, ,, thermodynamics...43
,, ,, ,, vapour pressure...74
Ostwald, affinities of acids...163, 164
,, contact difference of potential...120
,, dissociation theory...155, 171, 180
,, on Pickering's curves...208
,, osmotic pressure...69
,, solution of zinc in acids...115
,, vapour pressures...30, 90
,, volume changes in neutralisation...175

P.

Pellat, contact difference of potential...120
Peltier, contact difference of potential...117
Perkin, magnetic rotation in salt solutions...177
Pfeffer, osmotic pressure...34, 36, 39
Pickering, freezing points of solutions...71, 207, 213
,, theory of solution...207, 210, 211
Planck, theory of diffusion...46, 194
Planté, accumulator...114
Polarisation...112, 144, 146
,, in primary cells...114
Polymerisation of dissolved molecules...68
Potash, electrolysis of...105, 129
Potassium chloride and nitrate, solubility curves...2
,, isolation by electrolysis...105
Potential, contact difference of...116, 121, 160, 197
Practical applications of electrolysis...131
Pressure, influence on solubility...10, 13, 20
,, osmotic...32, 34, 39, 206
,, ,, and conductivity...165
,, ,, ,, freezing point...55, 67
,, ,, ,, thermodynamics...43
,, ,, ,, vapour pressure...74
Primary cells...114, 122, 198

Q.

Quincke, electrical endosmose...160

R.

Ramsay, vapour pressures of amalgams...93
Raoult, electromotive force of polarisation...113
,, freezing points of solutions...55, 57, 63, 172, 213
,, vapour pressures of solutions...77, 88
Rayleigh, Lord, and Mrs H. Sidgwick, Faraday's law...110
Reinold and Rücker, resistance of liquid films...158
Refraction coefficients of salt solutions...177
Regnault, solutions of liquids in gases...9
Resistance of electrolytes...143
,, ,, liquid films...158

Resistance, specific...148
Roscoe, distillation of solutions of hydrochloric acid...102
Rotatory power of salt solutions...177
Rücker and Reinold, resistance of liquid films...158
Rüdolf, freezing points of solutions...54
,, solubility of mixtures...80

S.

Sack, temperature of maximum conductivity...194
Salt solutions, properties of...174
Saturation...1, 18, 24, 187
Scheffer, experiments on diffusion...51
Secondary actions in electrolysis...128
,, cells...113
Self-induction with alternating currents...146
Semipermeable membranes...34, 179
Setschenoff, solubility of gases in solutions...15
Shaw, on electrolysis...110, 132
Sidgwick, Mrs H., and Lord Rayleigh, Faraday's Law...110
Sims, solubility of ammonia, &c....14
Sodium, isolation of...105
,, chloride, solubility curve...2
,, sulphate, solubility...19, 23
Solids, solutions in...6, 73
,, ,, ,, liquids...17
Solubility, conditions necessary for...17, 203
,, connection with dissociation...187
,, curves...2, 17, 23
,, in gases...8
,, ,, liquids of gases...10
,, ,, ,, liquids...16
,, ,, ,, solids...17, 187
,, table of...31
Solvent, conductivity of...129, 149, 200
,, function of ..18, 132, 156, 200, 203, 204
Solution pressure...21, 25, 34, 121, 199
Soret, diffusion...49
Specific inductive capacity of solvent...156, 204
Spectra of salt solutions...177
Stefan, theory of diffusion...51

Sugar solution...34, 40, 213
Sulphur dioxide, solubility of...14
Sulphuric acid, electrolysis of...130
Supersaturation...18, 24
Surface tension of solutions...25, 118, 177

T.

Tammann, isotonic solutions...38
,, melting points of alloys...73
,, osmotic pressures...39
,, vapour pressures...91
Telephone used as galvanometer...146
Temperature, its influence on conductivity...148, 176, 193, 202
,, ,, ,, diffusion...53
,, ,, ,, osmotic pressure...36, 45
,, ,, ,, solubility...1, 10, 16, 20, 25
,, of maximum conductivity...193
Tereschin, specific inductive capacities of solvents...205
Thermal capacities of solutions...177, 209
,, effects of chemical action...162, 189, 192
,, ,, ionisation...190, 206
,, ,, solution and dilution...3, 12, 28, 209
Thermodynamics of solutions...25, 43, 55, 74, 191
,, voltaic cells...122
Thomsen, thermochemical researches...122, 162, 190
Thomson, J. J., discharge through gases...105
,, function of the solvent...204
Thorium sulphate, solubility...23
Tilden, theories of solution...206, 209
Trouton and Fitzgerald, Ohm's law for electrolytes...151

V.

Van der Waals, formula for gases...69
Van 't Hoff, application of thermodynamics to solutions...43
,, diffusion...49
,, freezing points...59
,, gaseous laws applied to solutions...35
Vapour pressures of solutions...4, 74, 210
,, ,, ,, connection with boiling points...85

Vapour pressures of solutions connection with freezing points...84
,, ,, ,, ,, ,, osmotic pressures...75
Velocities of the ions...135, 138, 140, 154, 173, 196
Viscosity and conductivity...154
,, of salt solutions...177
Voigtländer, diffusion...48, 52
Völlmer, conductivity of alcohol solutions...203, 205
Volta's pile...103, 116
Voltaic cell...103, 113, 114, 122, 198
Volumes, molecular...174, 209

W.

Waage and Guldberg, chemical equilibrium...152, 189
Walker, heat of fusion...29
,, and Ostwald, vapour pressures...90
Water, conductivity of...129, 149, 200
,, decomposition of...104, 112, 129
,, dissociation of...200
,, heat of formation of...190
Weber, experiments on diffusion...48, 49
Whetham, velocities of the ions...141
,, ionisation powers of solvents...205
Wiedemann, electrical endosmose...160
,, resistance of electrolytes...144
Williamson, molecular interchanges...153
Wollaston, "galvanism"...105

Z.

Zinc, its solution in acids...115

CAMBRIDGE: PRINTED BY J. AND C. F. CLAY, AT THE UNIVERSITY PRESS.

Cambridge Natural Science Manuals.

BIOLOGICAL SERIES.

GENERAL EDITOR, A. E. SHIPLEY, M.A.,
Fellow and Tutor of Christ's College.

Now Ready.

Elementary Palæontology—Invertebrate	H. WOODS, B.A., F.G.S.	6*s.*
Elements of Botany	F. DARWIN, M.A., F.R.S.	6*s.*
Practical Physiology of Plants	F. DARWIN, & E. H. ACTON, M.A.	6*s.*
Practical Morbid Anatomy	H. D. ROLLESTON, M.D., F.R.C.P. & A. A. KANTHACK, M.D., M.R.C.P.	6*s.*
Zoogeography	F. E. BEDDARD, M.A., F.R.S.	6*s.*

In Preparation.

Fossil Plants	A. C. SEWARD, M.A., F.G.S.
Text-book of Physical Anthropology ...	A. MACALISTER, M.D., F.R.S.
The Vertebrate Skeleton	S. H. REYNOLDS, M.A.

PHYSICAL SERIES.

GENERAL EDITOR, R. T. GLAZEBROOK, M.A. F.R.S.,
Fellow of Trinity College, Cambridge, Assistant Director of the Cavendish Laboratory.

Now Ready.

Heat and Light	R. T. GLAZEBROOK, M.A., F.R.S.	5*s.*
,, ,, in two separate parts	,, ,,	*each* 3*s.*
Mechanics and Hydrostatics	,, ,,	
Part I. **Dynamics**	,, ,,	4*s.*
,, II. **Statics**	,, ,,	3*s.*
,, III. **Hydrostatics**	,, ,,	[*In Preparation*

In Preparation.

Electricity and Magnetism	R. T. GLAZEBROOK, M.A., F.R.S.
Solution and Electrolysis	W. C. D. WHETHAM, M.A.

Now Ready.

Elements of Petrology	A. HARKER, M.A., F.G.S.	7*s.* 6*d.*

Other volumes are in preparation and will be announced shortly.

5/5/95

Press Opinions.

BIOLOGICAL SERIES.

Elementary Palæontology—Invertebrate. By Henry Woods, B.A., F.G.S. With Illustrations. Crown 8vo. 6*s*.

Nature. As an introduction to the study of palæontology Mr Woods's book is worthy of high praise.

Saturday Review. The book is clearly and concisely expressed; it conveys much information in a comparatively small compass and cannot fail to be most useful to the student. Not only will it give him clear ideas upon the subject, but with it as a guide he will find his way more easily about the larger works or special memoirs on Palæontology, to the saving of his time and the increase of his knowledge.

Academy. It will be distinctly useful to any student entering on the study of geology.

Science and Art Journal. Geological students will find this admirable work on Invertebrate Palæontology easy reading, and thoroughly up-to-date.... We consider the book a most valuable addition to our scientific literature, and recommend it to all who desire to acquire a sound introduction to a knowledge of the past life-forms of our planet.

Practical Physiology of Plants. By F. Darwin, M.A., F.R.S., Fellow of Christ's College, Cambridge, and Reader in Botany in the University, and E. H. Acton, M.A., late Fellow and Lecturer of St John's College, Cambridge. With Illustrations. Crown 8vo. 6*s*.

Nature. A volume of this kind was very much needed, and it is a matter for congratulation that the work has fallen into the most competent hands. There was nothing of the kind in English before, and the book will be of the greatest service to both teachers and students..... The thoroughly practical character of Messrs Darwin and Acton's book seems to us a great merit; every word in it is of direct use to the experimental worker and to him alone.

British Medical Journal. This book will prove a valuable one for the student of practical botany..... The instructions for the study of these and similar facts in the botanical laboratory are set out with great clearness, and the figures illustrating apparatus used and tracings obtained are extremely good, and will greatly help the investigator who avails himself of the guidance of this work.

Glasgow Herald. Mr F. Darwin is well known as an authority on Botany, and the work before us will certainly prove a safe and satisfactory guide to the student in the botanical laboratory.... The directions for work are all clearly given, and for teachers possessing a laboratory a better students' guide to practical work in botany could not be found.

Natural Science. The text throughout is exceedingly clear, and the index full and carefully compiled.

Press Opinions.

BIOLOGICAL SERIES.

Practical Morbid Anatomy. By H. D. Rolleston, M.D., F.R.C.P., Fellow of St John's College, Cambridge, Assistant Physician and Lecturer on Pathology, St George's Hospital, London, and A. A. Kanthack, M.D., M.R.C.P., Lecturer on Pathology, St Bartholomew's Hospital, London. Crown 8vo. 6*s*.

British Medical Journal. The editor of the "Cambridge Natural Science Manuals" has been fortunate not only in the selection of the above-named subject but also in securing as authors Drs Rolleston and Kanthack..... This manual can in every sense be most highly recommended, and it should supply what has hitherto been a real want.

The Medical Chronicle. "This handbook is an attempt to supply a practical guide to the post-mortem room," say the authors in their introduction, and any competent reader will acknowledge that they have succeeded in their attempt. They have not only supplied the student with a large amount of reliable information, but have done it in a clear and very readable form.

PHYSICAL SERIES.

Heat and Light. An Elementary Text-book, Theoretical and Practical, for Colleges and Schools. By R. T. Glazebrook, M.A., F.R.S., Assistant Director of the Cavendish Laboratory, Fellow of Trinity College, Cambridge. Crown 8vo. 5*s*. The two parts are also published separately.

Heat. 3*s*. Light. 3*s*.

Nature. Teachers who require a book on Light, suitable for the Class-room and Laboratory, would do well to adopt Mr Glazebrook's work.

Science and Art. For the practical courses on Heat and Light now forming such a prominent feature in the curriculum of so many of our schools and colleges, these books are admirably suited.

Educational Review. Mr Glazebrook's great practical experience has enabled him to treat the experimental aspect of the subject with unusual power, and it is in this that the great value of the book, as compared with most of the ordinary manuals, consists.

Saturday Review. It is difficult to admire sufficiently the ingenuity and simplicity of many of the experiments without losing sight of the skill and judgment with which they are arranged.

Journal of Education. We have no hesitation in recommending this book to the notice of teachers.

School Guardian. It is no undue praise to say that they are worthy both of their author and of the house by which they are issued.

Teachers' Aid. Text-books of which it would be almost impossible to speak too highly.